A CONDUCTOMETRIC STUDY OF THE INFLUENCE OF CHLORO-, BROMO-, AND IODO- GROUPS ON THE REACTION VELOCITY OF 1-HALO-2,4-DINITROBENZENE WITH PIPERIDINE IN 95 PER CENT ETHANOL

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CHAPTER I

INTRODUCTION

The kinetics of a reaction refers to the velocity of chemical reactions as they approach equilibrium and the way the rates are affected by changes in temperature, solvent, concentration, catalysts, pressure, and radient energy. Research in this area has been directed toward determination of chemical mechanism as well as completing data on rates of specific reactions to use as a basis for further experimentation.[1]

Reaction rates, occur over a wide range of time from a matter of seconds to many weeks and longer. The intermediate reactions are more adequate for measuring reaction velocity. Reaction velocity is the quantitative rate of change in the reactants per unit time.

To measure reaction velocity, it is necessary to use indirect or direct means by either a chemical or physical process. In the chemical process, which is the more common type of analysis, it is necessary to determine the concentration of one of the reactants or products at the moment

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[1]Frank Thompson Gucker and William Buell Meldrum, Physical Chemistry (New York: The American Book Company, 1944), p. 281.

the sample is removed from the main solution. Therefore, the sample which is removed must be "frozen" immediately by dilution, rapid cooling, or by the addition of another reagent in excess and back titrating. The rate of change in a reaction may also be followed by determination of some physical property such as change of color to eye or instrument, change in refractive index, or by a change in electrical conductance.

Conductance measurements are useful in many physicochemical problems such as: (1) determination of solubilities, (2) degree of salt hydrolysis, (3) investigation of molecular complexes, (4) conductometric titrations, and (5) determination of reaction rate.[1] This study is concerned with the conductometric measurement of the reaction rate of 1-bromo-2,4-dinitrobenzene and 1-iodo-2,4-dinitrobenzene with piperidine in 95 per cent ethanol.

In the conductance method, one can detect the disappearance or addition of ions in a solution to determine reaction rate provided there be no appreciable reaction between the products or the reagents and the products for this would produce a nonlinear function.[2] Since the reaction

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[1]Duncan MacInnes, The Principles of Electrochemistry (New York: Reinhold Publishing Corporation, 1950), p. 375.

[2]Gucker, op. cit., p. 281.

between 1-halo-2,4-dinitrobenzene and piperidine forms 2,4 dinitrophenyl-piperidine, piperidinium ions, and halide ions, the reaction could be followed by a conductometric procedure. The reaction proceeds as follows:

$$C_6H_3(NO_2)_2X + 2\ C_5H_{11}N \longrightarrow C_6H_4(NO_2)_2C_5H_{10}N + C_5H_{12}N^+ + X^-$$

where X = fluorine, chlorine, bromine, and iodine.

In 1964, Charles O. Frank, a graduate student at Drake University did an interesting determination of the reaction rate of 1-chloro-2,4-dinitrobenzene and piperidine in 95 per cent ethanol by measuring the change in conductance over a period of time of a platinum electrode cell containing the reactants. The results of his analysis which determined the rate through the use of a physical property compared closely with rates obtained through chemical and spectral studies by other observers. Frank found that the physical determination by electrical conductance in an alternating circuit conveniently allowed a continuous monitoring of the system so measurements could be obtained at will.[1]

It was the purpose of this study to: (1) determine if the use of the Wheatstone bridge method used by Charles O. Frank was versatile enough to apply to other areas, (2) perform

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[1]Charles O. Frank, "A Conductometric Study of the Influence of Concentration and Temperature on the Reaction Velocity of 2,4-Dinitrochlorobenzene with Piperidine in 95 Per Cent Ethanol" (unpublished Master's thesis, Drake University, Des Moines, Iowa, 1964).

the experiment on a Model RC-18 Conductivity Bridge which would insure greater accuracy and convenience, (3) establish a halogen series for the reaction between 1-halo-2,4-dinitrobenzene and piperidine in 95 per cent ethanol, (4) prepare 1-iodo-2,4-dinitrobenzene for use in the project, (5) calculate the reaction energy and antrophy for the bromo- and iodo- substituted 2,4-dinitrobenzenes with piperidine, and (6) compare the results obtained by this physical method to the results obtained through other methods.

CHAPTER II

REVIEW OF THE LITERATURE

Electrochemistry first got its start in 1800, when William Nicholson and Sir Anthony Carlisle decomposed water with an electric current.[1] In 1807, Sir Humphrey Davy isolated the metals sodium and potassium from electrolysis of their fused hydroxides.[2] Baron C. J. von Grotthuss formulated his hypothesis regarding the mechanism of electrolysis in 1805. He believed that an instantaneous dissociation of molecules was caused by the electric current when it passed through a solution. The negative pole would attract the hydrogen from a water molecule causing the oxygen to take a hydrogen from an adjacent molecule which would continue to the positive pole where the oxygen atom would be liberated.[3]

Grotthuss' views met with some opposition and his theory of electrolytic conduction by a molecular chain was revised by Faraday and Hittorf. R. Clausius radically

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[1]Florian Cajori, A History of Physics (New York: The Macmillan Company, 1917), p. 135.

[2]Gucker, op. cit., pp. 314-315.

[3]Aaron J. Ihde, The Development of Modern Chemistry (New York: Harper and Row, 1964), pp. 131-132.

modified the Grotthuss theory in 1857 by denying the idea that the electric current breaks the molecules apart. A very large E.M.F. would be needed to do this which did not fit the experimental fact that even a small E.M.F. will produce decomposition. Instead, Clausius proposed that some of these particles already existed in the solution in an uncombined state. G. Quincke and F. Kohlrausch supported this idea and used the dissociation hypothesis to explain migration of ions and conductivity.[1] By using van't Hoff's work on osmotic pressures, Arrhenius showed further evidence that these particles did exist in the uncombined state in solution.[2]

Charles Wheatstone invented a bridge in 1843 that would measure resistances of solutions much more accurately. In this Wheatstone Bridge, one arm contained the cell with the solution of unknown resistance while the other arm contained known resistances which could be placed in the circuit as needed. A galvanometer was connected between the arms which would detect an unbalanced current whenever the resistances in the two arms was unequal. This null point method enabled the detection of small resistances since the current flowing through the galvanometer would be at a minimum when the bridge

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[1]Cajori, op. cit., pp. 217-218.

[2]M. M. Pattison Muir, A History of Chemical Theories and Laws (New York: John Wiley and Sons, 1909), p. 331.

was balanced. Kirchhoff added a slidewire to the bridge for even finer detection of cell resistances.[1]

Kohlrausch, in 1868, proposed that alternating current of low intensity, produced by an induction coil, be used in electrochemical work to eliminate polarization at electrode faces. With the reversal of a current at about 1,000 times per second, each pulse would be neutralized by a corresponding reversed pulse. He also replaced the galvanometer with telephone ear phones as a null point detector. Kohlrausch proposed coating electrodes of platinum with platinum black to reduce polarization effects produced by alternating fields.[2] Jones and Bollinger[3] found that polarization due to high frequency was negligible when a properly designed cell was used. They also found that a small trace of lead acetate added to the chloroplatanic acid solution used in electroplating kept the platinum black from flaking.[4]

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[1]Cajori, op. cit., pp. 232-233.

[2]Samuel Glasstone, An Introduction to Electrochemistry (New York: D. Van Nostrand Company, Inc., 1942), pp. 32-35.

[3]Grinnell Jones and Dorothy Bollinger, "The Measurement of the Conductance of Electrolytes. VII. On Platinization," Journal of the American Chemical Society, LVII (1935), 280.

[4]Grinnell Jones and Dorothy Bollinger, "The Measurement of the Conductance of Electrolytes. III. Design of Cells," Journal of the American Chemical Society, LIII (1931), 411.

Hovorka and Mendenhall[1] found that a cathode-ray tube for a detector was better adapted than ear phones for work involving a large number of measurements and was as sensitive as previous detectors.

In 1850, the first kinetics experiment was performed by Ludwig Wilhelmy. Using a polarimeter, he observed the change in rotation of sucrose from dextrose to levulose by inversion with hydrochloric acid. Wilhelmy found the rate of inversion was proportional to the concentration of dextrose at any time during the reaction. In 1860, Berthelot and St. Gilles used rate studies on hydrolysis of esters. In 1866, Harcourt showed the oxidation of iodic acid by peroxide is a first order reaction proportional to the concentration of iodide. He also studied the reduction of potassium permanganate by oxalic acid. Van't Hoff had studied mixtures of gases and liquids by 1884 and found that an increase in temperature would favor the endothermic reaction.[2] Kohlrausch[3] in 1874 showed that conductivity of a solution increases linearly with an increase in temperature.

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[1]Frank Hovorka and Elwyn E. Mendenhall, "A Cathode-Ray Tube Alternating Current Bridge Detector for Conductivity Measurements," Journal of Chemical Education, XVI (1939), 239-241.

[2]Ihde, op. cit., pp. 406-407.

[3]Fredrick Kohlrausch, "The Relation Between Temperature and Conductivity of Solutions," Z. Physik Chem., LVIII (1907), 630; Chemical Abstract, Volume 1 (1907), 2761.

Le Chatelier found that a change in temperature or pressure would cause a shift in equilibrium in the direction that would relieve the strain on the system.[1]

In 1888, Negreano[2] followed the rate of reaction between ethanol and acetic acid by noticing the change in the resistance of the solution. Price[3] determined the reaction rate between ethanol and hydrochloric acid by a conductometric process. Rivett and Sidgwick[4] in 1910 and Greenberg[5] in 1962 studied the hydrolysis of organic acids by their conductivity in a solution. Cody and Lictenwalter[6] studied the reactions between silver melissilate, lead stearate, copper oleate, and others with hydrochloric acid in benzene for the first conductometric study with an organic solvent. Other conductometric determinations of

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[1] Ihde, op. cit.

[2] Negreano, "Velocity of Etherification Determined by Means of Electrical Conductance," Journal of the Chemical Society, LIV (1888), 1025.

[3] Thomas Slater Price, "The Reaction of Ethyl Alcohol and Hydrochloric Acid," Journal of the Chemical Society, LXXIX (1901), 303.

[4] Albert Rivett and Nevil Sidgwick, "The Rate of Hydration of Acid Anhydrides: Succinic, Methylsuccinic, Itaconic, Maleic, Citraconic and Phthalic," Journal of the Chemical Society, XCVII (1898), 677.

[5] David B. Greenberg, "Reaction Kinetics from Conductivity Data," Journal of Chemical Education, XXXIX (1962), 140.

[6] H. P. Cody, and H. O. Lictenwalter, "Chemical Reactions and Electrical Conductivity of Non-aqueous Solutions," Journal of the American Chemical Society, XXXV (1913), 1434.

reaction rates are: (1) nitroethane with water and with deuterium oxide[1], (2) saponofication of esters[2], (3) reaction between 1-chloro-2,4-dinitrobenzene and piperidine in ethanol[3], and (4) solvolysis of tertiary butyl chloride[4], (5) alkyl halides with potassium iodide in acetone[5], and (6) diphenylchloromethane and ethanol.[6] All of the conductometric reactions mentioned above were determined by measuring the resistance change due to a change in ionic content of solution with time.

Opstall[7], in 1933, reacted 1-chloro-2,4-dinitrobenzene

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[1]Samuel H. Maron and Victor K. LaMer, "Kinetics of Isomerization of Aci to Nitro Forms of Nitroethane in Water and Deuterium Oxide," Journal of the American Chemical Society, LXI (1939), 692.

[2]Gucker, op. cit., p. 281.

[3]Frank, op. cit., p. 1.

[4]John Chesick and A. Patterson, Jr., "Determination of Reaction Rates With an A.C. Conductivity Bridge," Journal of Chemical Education, XXXVII (1960), 242.

[5]Brynmar Jones and D. J. Worsfold, "Determination of Reaction Rates by Conductivity Measurements," Nature, CLXVII (1951), 1072.

[6]James F. Norris and Avery A. Morton, "The Reactivity of Atoms and Groups in Organic Compounds. III. First Contribution on the Carbon-Chlorine Bond: The Rate of Reaction Between Diphenylchloromethane and Ethyl Alcohol," Journal of the American Chemical Society, L (1928), 1795.

[7]H. J. Opstall, "Reaction Velocity of 1-Chloro-2,4-dinitrobenzene and 1-Chloro-2,4-dinitronaphthalene with Aromatic Amines," Recueil des travaux chimiques des Pays-Bas, LIII (1933), 901-911; Chemical Abstract, Volume 28 (1934), 26.

with piperidine and by a volumetric titration of chloride with silver nitrate, found the reaction to be second order. Since that time, many related reactions involving piperidine and other reagents have been performed on the nitro and halo substituted aromatic compounds. Some examples are as follows: halo-2,4-dinitrobenzenes- (1) with N-methylaniline in ethanol and in nitrobenzene[1], (2) with aromatic primary amines[2], (3) with benzoate[3], (4) with piperidine in dioxane, ethanol, and methanol[4,5], (5) with piperidine and no solvent[6], and

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[1]George S. Hammond and Lawrence R. Parks, "The Displacement of Halogen from 1-Halo-2, 4-dinitrobenzenes," Journal of The American Chemical Society, LXXVII (1955), 340-343.

[2]Attar Singh and D. H. Peacock, "The Reactivity of Halogen Compounds. II. The Rates of Reaction and Energies of Activation of 2,4-Dinitrochlorobenzene with Aromatic Primary Amines," Journal of Physical Chemistry, XL (1958), 669-678.

[3]Lawrence R. Parks, George S. Hammond, and Frederick Hawthorne, "Substituent Effects on the Reactions of Benzoate ions with 2,4-dinitrochlorobenzene and methyl iodide," Journal of the American Chemical Society, LXXVII (1955), 2903-2904.

[4]J. F. Bunnett and R. J. Morath, "The Rates of Condensation of Piperidine with 1-Chloro-2,4-dinitrobenzene in Various Solvents," Journal of the American Chemical Society, LXXVII (1955), 5165.

[5]Ernst Berliner, "Nucleophilic Displacement in the Benzene Series," Journal of the American Chemical Society, LXXIV (1952), 1574-1579.

[6]J. F. Bunnett and George T. Davis, "Kinetics of Reaction of 2,4-Dinitrochlorobenzene with some Familiar Nucleophilic Reagents," Journal of the American Chemical Society, LXXVI (1954), 3011-3015.

(6) with sulfite in aqueous ethanol[1]; halo-nitrobenzenes- (1) with piperidine in benzene[2,3], (2) with piperidine in dioxane, methanol, and ethanol[4], (3) with piperidine in xylene[5], and (4) with sodium methoxide in methanol[6]; the halonaphthalenes and halonitronaphthalenes- (1) with piperidine in ethanol[7], and (2) with piperidine and no

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[1]M. A. Adeniran, C. W. L. Bevan, and J. Hirst, "Aromatic Nucleophilic Replacement. Part IX. The Reaction of 1-Halo-geno-2,4-dinitrobenzenes with Sulfite Ion in Aqueous Ethanol," Journal of the Chemical Society, (1963), 5868-5872.

[2]W. Greizerstein, R. A. Bonelli, and J. A. Brieux, "Polar Effects of Substituents on Reaction Rates of 4-R and 5-R-2-Nitrochlorobenzenes with Piperidine in Benzene," Journal of the American Chemical Society, LXXXIV (1962), 1026-1032.

[3]Jorge A. Brieux and Venancio Deulofew, "The Reaction of Halonitrobenzenes with Piperidine," Chemistry and Industry, (1951), 971.

[4]J. F. Bunnett and R. J. Morath, "The Ortho-Para Ratio in Activation of Aromatic Nucleophilic Substitution by the Nitro Group," Journal of the American Chemical Society, LXXVII (1955), 5051-5055.

[5]B. M. F. Hawthorne, "The Question of Hydrogen Bonded Transition States in Nucleophilic Aromatic Substitution Reactions," Journal of the American Chemical Society, LXXVI

[6]J. F. Bunnett, "A New Factor Affecting Reactivity in Bimolecular Nucleophilic Displacement Reactions," Journal of the American Chemical Society, LXXIX (1957), 5969-5974.

[7]Paolo Beltram and Massimo Simonetta, "Kinetics of the Reaction between Piperidine and Halonitronaphthalenes. IV. Gazzetta chimica italiana, XCII (1962), 351-364; Chemical Abstracts, Volume 55, (1961), 6478.

solvent.[1,2] The kinetics for the reactions above have been determined by volumetric or spectrophotometric methods but not by a conductometric process.

G. M. Bennett[3] synthesized 1-iodo-2,4-dinitrobenzene in 1939 by adding 1-chloro-2,4-dinitrobenzene and sodium iodide to ethylene glycol and heating for 30 minutes. Only a 30 per cent yield was obtained. Bunnett and Conner[4] found that 1-iodo-2,4-dinitrobenzene could be synthesized in a 70 per cent yield by using N,N'-dimethylformamide instead of ethylene glycol. They also observed that the percentage yield decreased with longer periods of reflux.

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[1]Ernst Berliner, Margaret Quinn, and Patricia J. Edgerton, "Nucleophilic Displacement in the Naphthalene Series," Journal of the American Chemical Society, LXXII (1950), 5305-5308.

[2]K. R. Brower and E. D. Amstutz, "Halogen Reactivities. II. Kinetic Study of Displacement Reactions of Bromo-naphthalenes with Piperdine," Journal of Organic Chemistry, XVIII (1953), 1075-1078.

[3]G. M. Bennett and Ida H. Vernon, "Reversible Replacement of Aromatic Halogen Atoms," Journal of the Chemical Society, (1938), 1783-1786.

[4]J. F. Bunnett and R. M. Conner, "Improved Preparation of 1-Iodo-2,4-Dinitrobenzene," Journal of Organic Chemistry, XXIII (1958), 305-306.

CHAPTER III

EXPERIMENTAL DESIGN AND CALCULATIONS

I. EXPERIMENTAL DESIGN

In the determination of the rate of reaction, the problem was to measure the change in conductivity of a cell containing the reagents after known times had elapsed from a zero time. To obtain the Arrhenius parameters the concentrations were varied over a range of 0.0389 moles per liter and the temperatures were varied over a range of forty degrees Centigrade.

Apparatus and preliminary work. In this project, a Model RC-18 Conductivity Bridge from Industrial Instruments, Incorporated was employed. This instrument has a Wheatstone bridge circuit complete with an oscilloscope detector, A.C. circuitry for either 1000 or 3000 cycles, decade dials allowing a cell maximum of 111,111.1 ohms resistance or 11,111.11 micromhos conductance, a switch so that resistance or conductance can be measured directly from the bridge, a sensitivity regulator, a Wagner ground, coarse and fine variable capacitors to balance cell capacitance and thereby insure easier and more accurate readings at higher sensitivities, and an instrument ground to eliminate some of the stray fields that would otherwise cause disturbances on the

oscilloscope and contribute to a loss of sensitivity in the instrument readings.

According to the instruction manual, the instrument is capable of giving readings with precision up to 0.1 per cent.[1]

A double throw switch was placed in the leads between the instrument and the cells so that readings could be taken from either of the two cells without removing the leads from the cells. All the leads were made as short and kept as far apart as possible. The leads were shielded with woven copper shielding which was grounded to the water pipe. It was noticed that without the shielding that readings with the sensitivity on only one-half of the full scale were virtually impossible to take.

The cells used were of the Kohlrausch type. Cell 1 was designed for medium conductances as its electrodes were small, circular, and far apart. Cell 2 was designed for low conductances as its electrodes were large, curved rectangular, and close together. The Fisher Catalog[2] lists two cells which correspond to the cells used in this study.

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[1] Industrual Instruments Inc., Instruction Manual, (Cedar Grove, New Jersey, 1965), p. 2.

[2] Fisher Scientific Company, Fisher Modern Laboratory Appliances, (New York: Fisher Scientific Company, 1964), p. 442.

Cell 1 (Catalog No. 9-367) has a cell constant of approximately 1.3 reciprocal ohm-centimeters while cell 2 (Catalog No. 9366) has a cell constant of nearly 0.17 reciprocal ohm-centimeter. Both cells were equipped with mercury filled arms to provide the contact between the electrodes and the outside leads.

The constant temperature baths employed were of two types: the vapor type and the mercurial thermoregulator type. The vapor type used a volatile liquid vapor thermostat which was employed for the 25.0° readings with the 1-iodo-2,4-dinitrobenzene and the 1-chloro-2,4-dinitrobenzene. This bath contained a 750 watt heating coil which had to be balanced by a cold tap water coil. The Mercurial Thermoregulator was employed for the 25.0° readings of the 1-bromo-2,4-dinitrobenzene reactions, and all 40.0° readings taken. Equipment used for this bath was a Sargent Constant Temperature Water Bath (Catalog no. S-84805) equipped with a Mercurial Thermoregulator (Catalog No. S-81840) and a Thermocontroller (Catalog No. S-81995) which has heating coils of 400 watts, 300 watts, and 250 watts for finer control of the temperature. The water was circulated by stirrers to keep the water at a constant temperature in the bath. When the temperature of the tap water was in excess of twenty-five degrees, it was cooled in an ice bath before being introduced into the coil inside the bath.

For the 0.1° Centigrade temperature bath, an ice-water mixture was constantly stirred in a fiber glass insulated bath with ice being added in generous portions to keep the temperature constant.

During the course of the project, the mercury arms had to be cleaned periodically to prevent high resistance that would cause erroneous readings. Rubber policemen were placed over the top of the arms to prevent the mercury from falling out while changing the solutions. Apparently the sulfur from the rubber policemen contributed to the bad contacts, as what appeared to be mercury sulfide distributed itself throughout the arms of the cell. This was later avoided by replacing the rubber policemen with small pieces of polyethylene tubing which fit directly into the arms. To clean the arms, the mercury was discarded and dilute nitric acid was introduced and allowed to react until the solution had stopped effervescing. The arms were washed with distilled water and acetone and allowed to dry by placing a small hypodermic needle connected to a vacuum into each arm for at least five minutes. Fresh mercury was then placed in the cell arms.

Platinum electrodes in an A.C. circuit are subject to polarization effects which can be eliminated by a fine coat of platinum black on the electrodes. To platinize the electrodes, the cells were cleaned with a solution of aqua

regia until the electrodes appeared to be clean. They were then washed thoroughly with distilled water and the cell was filled with a prepared aqueous solution of 3 per cent chloroplatininc acid which contained a trace (0.02 per cent) of lead acetate.[1] To electroplate the platinum black to the electrodes, two 1.5 volt dry cells were used with a rheostat and an ammeter to regulate the current to a few tenths of an ampere. The current was reversed every thirty seconds to plate both electrodes evenly. Following the plating, the cells were rinsed seven times with six normal sulfuric acid. Finally, on the last filling with acid, the cells were placed in the direct current circuit which was reversed every minute for thirty minutes to remove any chlorine gases which might be present in the electrodes from the aqua regia or platinizing solutions. The cells were rinsed at least four times with distilled water and allowed to remain at room temperature for at least four hours.[2]

Determinations of cell constants. The cell constant is a property of a cell which is dependent upon the area of the electrodes and the distance between them. To check the reproducibility of the system, the cell constant was

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[1]Grinnell Jones and Dorothy M. Bollinger, "The Measurement of the Conductance of Electrolytes. VII. On Platinization," Journal of the American Chemical Society, LVII (1935), 283.

[2]Frank, op. cit., p. 15.

determined both before and after the reaction rates were run in the cells.

Conductivity water was prepared by redistilling distilled water containing a few crystals of potassium permanganate to oxidize any organic matter present and collecting it while still warm in a polyethylene bottle. The water was used to make up solutions of o.1000 molar potassium chloride which was diluted to 0.0100, 0.0050, and 0.001 moles per liter. These salt solutions were also stored in polyethylene bottles.

The cell constant K is given by the equation: K = LR where L is the specific conductance of the particular ions present and R is the resistance of the solution. The specific conductance is defined as the conductance of the material between parallel plates one square centimeter in area and one centimeter apart.[1]

The specific conductances for standard potassium chloride solutions at 25.0° C. are given in Table I.[2]

The cells were kept filled with conductivity water both before and after using the aqueous salt solutions and had to be rinsed three times with each concentration before

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[1]Gucker, op. cit., pp. 384-385.

[2]Samuel Glasstone and David Lewis, Elements of Physical Chemistry (Princeton, New Jersey: D. Van Nostrand Company, Inc., 1960), pp. 429 and 433.

TABLE I

THE SPECIFIC CONDUCTANCES OF VARIOUS CONCENTRATIONS OF POTASSIUM CHLORIDE AT 25° C.

Concentration of Potassium Chloride in moles per liter	Specific Conductance in mhos per cm.
0.00100	0.0001469
0.00500	0.0007175
0.01000	0.001413

using. The cells were filled with the prepared solutions of potassium chloride beginning with the most dilute and were placed in the 25.0° bath. The wire leads were inserted into the mercury arms and were left until the temperature in the cell allowed the readings to become nearly constant. After temperature equilibrium was reached, as shown by nearly constant readings, ten readings were taken on each of four different solutions at each concentration and the average resistances were used to calculate the cell constant for each cell. Since R = 1/C where R is the resistance and C is the conductance, it was possible to check the conductivity bridge scales for reproducibility of these scales. Multiplication of the values obtained on the two scales showed consistancy to five parts per ten-thousand which was considered to be accurate enough for this study.

Following the determination of the cell constants, the volumes of the cells were found so that a constant amount of prepared solution might be used in each cell. The capacity for cell 1 was 40.0 milliliters where cell 2 had a capacity of 28.0 milliliters.

The 1-chloro-2,4-dinitrobenzene reaction. In order to become acquainted with the instrument and check the reproducibility of Frank's work on the conductivity bridge, his 1-chloro-2,4-dinitrobenzene solutions were prepared and reacted with piperidine.

The piperidine solutions were prepared so that ten milliliters contained the desired number of moles. The 1-chloro-2,4-dinitrobenzene was prepared so that the 30.0 milliliters in cell 1 and 18.0 milliliters in cell 2 contained the desired number of moles.

The number of moles used in both cells was 0.001 moles, 0.002 moles, and 0.0025 moles which corresponded to 0.0333, 0.0667, and 0.0833 moles per liter in cell 1, and 0.0358, 0.0716, and 0.895 moles per liter in cell 2. The piperidine was prepared so that twice the number of moles of piperidine would be present in the cell to react with the 1-halo-2,4-dinitrobenzene in a second order reaction.

Reagent grade 1-chloro-2,4-dinitrobenzene was recrystallized from ethanol giving a melting point of 51° C. Each solution was prepared by adding the solid reagent to a

250 milliliter volumetric flask with approximately 150 milliliters of 95 per cent ethanol and heated slightly on a steam bath to get the solid into solution. The solution was cooled to twenty degrees and diluted to the mark. Piperidine was weighed out and placed in a 250 milliliter volumetric flask at twenty degrees and diluted to the mark with ethanol. The solutions of 1-chloro-2,4-dinitrobenzene were stored in polyethylene stoppered glass bottles while the piperidine solutions were stored in the volumetric flasks.

In making runs, the following procedure was used: To the cells were added the proper volumes of 1-chloro-2,4-dinitrobenzene solution to 30.0 ml. to cell 1 and 18.0 ml. to cell 2. The cells were brought to constant temperature at 25.0° C. A ten milliliter hypodermic syringe was filled with piperidine solution and immersed in the bath for at least ten minutes. Before immersion, the end of the needle was fitted with a small piece of plastic tubing to prevent water from entering the syringe. The syringe was then removed from the water and wiped dry with an absorbent towel. The solution was injected into the cell carefully to avoid air bubbles, which would cause errors in the first few readings. A stopwatch, graduated to one-tenth of a second, was started as the cell was injected and readings were taken at preset conductances for times less than one minute at 25.0° and 40.0° C. The stopwatch was used for readings up

to thirty minutes and a wrist watch was used for longer times.

The 1-iodo-2,4-dinitrobenzene reaction. The method of Bunnett and Conner[1] was used in preparing 1-iodo-2,4-dinitrobenzene. In the preparation, 200 ml. of N,N'-dimethylformanide, 150 grams of sodium iodide, and 40.5 grams of 1-chloro-2,4-dinitrobenzene were refluxed for fifteen minutes over a flame. The hot mixture was then poured over ice and the brown precipitate was collected and recrystallized three times from 95 per cent ethanol. This procedure was followed twice with a result of nearly 75 grams of pure 1-iodo-2,4-dinitrobenzene with a melting point range from 86 to 89 degrees. Bunnett and Conner report 88.5 to 90 degrees.[2] An An I-R spectrograph was run with the 1-iodo-2,4-dinitrobenzene as a solid in Nujol with no distinct traces of any impurities present. The solubility of the above compound in 95 per cent ethanol at 0.1° C. was determined by extracting a ten milliliter quantity from a saturated solution at that temperature and evaporating it to dryness on a steam bath. The limiting solubility for 1-iodo-2,4-dinitrobenzene was found to be 0.06 moles per liter which meant that the

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[1]Bunnett and Conner, op. cit., 305.

[2]Ibid., 306.

solutions had to be made more dilute than the concentrations used in preparing the 1-chloro-2,4-dinitrobenzene.

The solutions of 1-iodo-2,4-dinitrobenzene were prepared to contain 0.00050, 0.00075, and 0.00100 moles per volume of each cell. For cell 1, the concentrations were 0.0167, 0.0250, and 0.0333 moles per liter. For cell 2, the concentrations were 0.0278, 0.0417, and 0.0556 moles per liter. Piperidine was prepared as before using 0.0010, 0.0015, and 0.0020 moles per ten milliliters.

The procedure for the reaction was the same as before except that much longer times were needed in following the reaction due to the reduced concentration and the lower reactivity of 1-iodo-2,4-dinitrobenzene. The time followed during the course of a reaction ranged from 1½ hours at 40.0° to 12 hours at 0.1°. In order to obtain some consistance in time followed, each reaction was run at least to its half life. A half-life is the time it takes for half of the initial number of molecules to react.

At 0.1°, since such a long period of time was needed, a procedure was devised so that the four runs made for each concentration might be accomplished in one day. The reactions were run four times in each cell up to 1½ hours so that the major course of the reaction would not be subject to slight errors in temperature. For the time values two hours and above, four solutions for each of two cells were

prepared by injecting the proper pre-cooled piperidine solution into a 50 ml. flask containing the corresponding solution of 1-iodo-2,4-dinitrobenzene. The injections were alternated from the solution of one cell to that of the other with intervals of five minutes to allow time to change solutions and obtain the readings. All solutions were stored on ice and kept in a refrigerator until they were taken out, one at a time, and poured into the cell. The only times the solutions were not in ice water were when they were being transferred from the flask to the cell and back.

At 40.0°, the same procedure as used for the 25.0° reactions was followed except that three readings were taken before one minute had elapsed because the reaction time was much shorter. To help the heating coil balance the higher temperature, a jacket of wrapping paper was used as insulation.

The 1-bromo-2,4-dinitrobenzene reaction. The 1-bromo-2,4-dinitrobenzene was obtained commercially and was not examined further but was used directly in making the solutions. The solubility of the compound at 0.1° C. in 95 per cent ethanol was determined in the same manner as described in the previous section. The limiting solubility was found to be 0.107 moles per liter which is only slightly greater than that of the 1-iodo-2,4-dinitrobenzene compound.

Solutions were made to be the same concentrations as with the previous reaction, namely, 0.00050 moles, 0,00075 moles, and 0.00100 moles per volume of the cell. The actual concentrations prepared for cell 1 were 0.0167, 0.0250, and 0.0333 moles per liter. For cell 2, the concentrations were 0.0278, 0.0417, and 0.0556 moles per liter. Fresh piperidine was prepared as before making solutions up as 0.0010 moles, 0.0015 moles, and 0.0020 moles per 10 milliliters. The reaction was again run at 0.1°, 25.0°, and 40.0° in the same manner as described above except that the special procedure at 0.1° was not used as the reaction took place in a reasonable time.

The conductance of the solution at zero time is dependent upon the concentration of the two reactants. To determine this, each of the reactants were placed in the cell separately and diluted with ethanol to the desired cell volume. Since most of the conductance was found to be due to the piperidine, the zero time conductances were taken entirely from the values obtained from the piperidine solutions.

The infinity conductances had to be obtained after each reaction had been completed. Although, theoretically, this should be taken after the reaction has gone to completion, a value may be obtained after a reasonable period of several half-lives have elapsed which are within the range

of experimental error. The time range on infinity conductances was from a matter of hours to a week depending on concentration and temperature. At 0.1°, solutions were stored in a refrigerator for nearly two weeks for the more dilute solutions. At 25.0° and 40.0°, solutions were stored in the temperature bath for at least two days for the 25.0° and one day for the 40.0° reactions. Infinity readings were taken on several solutions at each concentration and temperature to determine an estimate of the error present. At 0.1°, solutions of the higher concentrations had some crystals present which had to be dissolved by heating before introduction into the cell. This, of course, disturbed the equilibrium which varies with temperature, but it was supposed that this error would be within the experimental range.

Having completed the investigation, the cell constants were rechecked by using the potassium chloride solutions described above to determine the reproducibility of the measurements.

II. CALCULATIONS

The velocity of a reaction as stated before is the change in concentration of a substance per unit time. This can be expressed by the derivative: dc/dt where dc is the change in concentration of one of the reactants and dt is the change in time. The reaction velocity is proportional

to the concentrations of the reactants and can be equated to these concentrations provided a constant is inserted into the relationship. This constant, k, known as the specific reaction rate, rate constant, or rate coefficient, is numerically equal to the reaction rate when the reactants are at unit concentration. The rate constant has the dimensions of $(\text{moles/liter})^{1-n}\ \text{sec}^{-1}$ where n is the order of reaction.[1] The order of a reaction is the number of concentration factors which affect the rate. In a second order reaction, for example, the rate is governed by the number of atoms or molecules of each substance present if two reactants are used and the square of the concentration if only one substance is used. Such a reaction is said to be bimolecular.[2]

The reaction between 1-halo-2,4-dinitrobenzene and piperidine in 95 per cent ethanol has been found to be of second order.[3] The reaction proceeds in two steps with the rate and order being determined by the first step.

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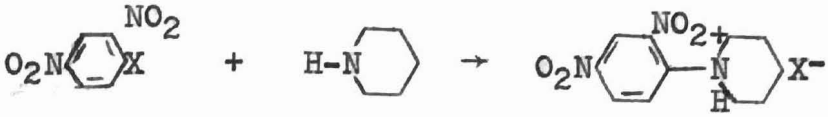
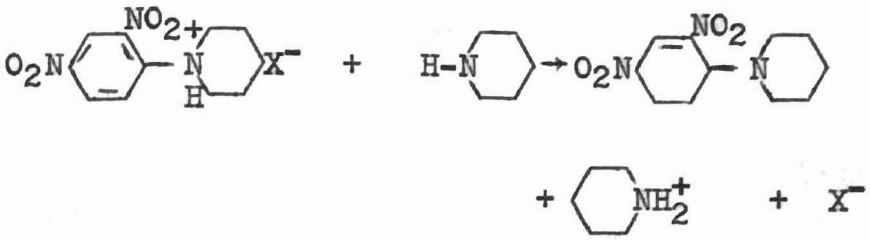
[1]Keith J. Laidler, Chemical Kinetics (New York: McGraw-Hill Book Company, Inc., 1950), pp. 3-4.

[2]Gucker, op. cit., p. 283.

[3]J. F. Bunnett and H. D. Crockford, "A Versatile Experiment in Reaction Kinetics for the Physical Chemistry Laboratory," Journal of Chemical Education, XXXII (1956), 556.

Step I. 

Step II: 

where X is the halogen substituent. The rate for a reaction of this type can be expressed as:

$$\frac{dx}{dt} = k(a-x)(b-2x)$$

where x is the concentration of either of the products,
t is the time during the reaction,
a is the initial concentration of 1-halo-2,4-dinitrobenzene,
and b is the initial concentration of piperidine.

It should be noted here that the symbols (a-x) and (b-2x) are simply other forms for the concentrations of the respective reactants at any time t during the reaction.

Since two molecules of piperidine are involved in the reaction, the mathematics of the rate equation may be simplified by having the initial concentration of piperidine as twice that of the 1-halo-2,4-dinitrobenzene, i. e., to have b=2a. Then the above expression becomes:

$$\frac{dx}{dt} = k(a-x)(2a-2x) \text{ or}$$
$$= 2k(a-x)^2 .$$

Rearranging this equation, one finds:

$$\frac{dx}{(a-x)^2} = 2k\ dt\ ,$$

which integrates to:

$$\frac{1}{a-x} = 2kt + \frac{1}{a}\ ,$$

where 1/a is the constant of integration. The integrated equation is now linear and a plot of the concentration (a-x) versus time would yield a slope of 2k.

Since the change in the reactants produces a change in the number of ions in the solution, conductivity can be employed to measure this change in concentration. The conductance of any solution in dependent upon the amount and the species of each ion present. The equivalent conductance (Λ) is the quantity which represents the conducting power of the ions produced by one gram equivalent of electrolyte per liter of solution and can be expressed by the equation:

$$\Lambda = 1000\ L/c,$$

where L is the specific conductance of the ions present and c is the concentration in gram-equivalents per liter. Since the specific conductance equals the cell constant (K) multiplied by the conductance (C), the above expression becomes:

$$L = \Lambda c/1000 = KC$$

or $\Lambda c/1000\ K = C$.

Kohlrausch, in 1875 found that "at infininite dilution, each ion makes a definite contribution toward the equivalent conductance of an electrolyte irrespective of the nature of the other ion with which it is associated in the solution."[1] Therefore, since the equivalent conductance at infinite dilution is due to each ionic species, it can be shown from the above equation that:

$$C = \frac{1}{1000\ K}\ (c_1 l_1 + c_2 l_2 + c_3 l_3 + \text{-------} +),$$

where c_n is the concentration in gram-equivalents per liter for each species (n= 1,2,3,----),
l_n is the equivalent ionic conductance for each ion (n = 1,2,3,----),
K is the cell constant,
and C is the total conductance of the solution.

In the reaction between 1-halo-2,4-dinitrobenzene and piperidine, the three conductances and their equivalents that must be determined are:

$$C_o = (a_1 l_1)/1000\ K,$$

$$C_t = \left((2a-2x)_1 l_1 + x_2 l_2 + x_3 l_3 + x_4 l_4\right)/1000\ K,$$

and $$C_\infty = (x_2 l_2 + x_3 l_3 + x_4 l_4)/1000\ K,$$

where C_o is the conductance of the cell at time zero,
C_t is the conductance of the cell at time t,
C_∞ is the conductance of the cell at equilibrium,
subscript 1 signifies the conductance of the piperidine,
subscript 2 signifies the conductance of the product 2,4-dinitrophenylpiperidine,

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[1] Glasstone and Lewis, op. cit., p. 441.

subscript 3 signifies the conductance of the product piperidinium,
and subscript 4 signifies the conductance of the product halide ion.

By subtracting C_o from both C_t and C_∞ and by a division of the proper terms, an expression is obtained in which the cell constant and equivalent ionic conductances are eliiminated leaving:

$$\frac{C_t - C_o}{C_\infty - C_o} = \frac{x}{a},$$

where x is the product concentration and a is the initial concentration of 1-halo-2,4-dinitrobenzene reagent. The term $C_t - C_o / C_\infty - C_o$ is a ratio term that expresses the change in conductance as a function of the change in concentration of the reagents. Solving the above equation for x and substituting into the integrated rate equation, one obtains:

$$\frac{C_\infty - C_o}{C_\infty - C_t} = 2kat + 1,$$

showing that the rate of reaction can be determined through the measurement of conductivity. Therefore, a plot of the conductance ration $C_\infty - C_o / C_\infty - C_t$ against time in minutes should give a line with slope of 2ka and a y-intercept of 1. Since all points are subject to some experimental error, the method of least squares was used to find the best line through the plotted points.[1] A computer was employed to find the

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[1]Hugh Young, Statistical Treatment of Experimental Data (New York: McGraw-Hill Book Company, 1962), p. 121.

slopes and y-intercepts for all data. It was programed to "read" n as the number of points, "read" an x term followed by a y term, repeat for n number of x's and y's, and obtain the desired quantities by substitution into the following equations:

$$\text{y-intercept} = \frac{\sum(y)\sum(x^2) - \sum(xy)\sum(x)}{n\sum(x^2) - (\sum x)^2}$$

$$\text{slope} = 2ka = \frac{n\sum(xy) - \sum x \sum y}{n\sum x^2 - (\sum x)^2}$$

where x is the time in minutes,
y is the conductance ratio $(C_\infty - C_o / C_\infty - C_t)$,
and n is the number of points.

The errors in measurement of the conductance for a series of four runs was expressed by the use of variance and the 95 per cent confidence interval. Standard deviation is not reliable when so few readings are taken as it is based on an infinite number of readings.[1] When the variance and 95 per cent confidence interval are used for small numbers of measurements, the results are usually more reliable. The variance (s_m) is related to standard deviation (s) by the expression $s_m = s/\sqrt{N}$, where N is the number of determinations. Another estimate of error, the 95 per cent confidence interval (s_w) is symbolized by $s_w = w\, k_w$, where the width of the interval (w) is simply the highest reading minus the

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[1] Ibid., pp. 15-18.

lowest reading. The factor, k_w, for 95 per cent confidence is 0.89, 0.59, 0.49 and 0.43 for two, three, four and five readings, respectively.[1] One can see from the values, as more readings are taken, the factor becomes less. For time less than one minute, the error had to be expressed in fractions of a minute because pre-set conductances had to be used to follow the reaction. However, these fractions of numutes were converted into conductance terms by finding the corresponding rate of change in conductance per change in conductance per change in time.

The half-life of a reaction can be defined as the time required for one-half of the original number of molecules to react. Mathematically, the half-life can be determined by substituting $\frac{1}{2}a$ for x in the integrated rate equation. The result is:

$$\frac{1}{2ka} = t_{\frac{1}{2}} = \frac{1}{\text{slope}}$$

where $t_{\frac{1}{2}}$ is the time required for one half-life period.

Van't Hoff, in 1884, showed clearly the relationship between temperature and its effect on the rate of reaction and the equilibrium point.[2] This was formulated a few

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[1] R. B. Dean and W. H. Dixon, "Simplified Statistics for Small Numbers of Observations," Analytical Chemistry, XXIII (1951), 636.

[2] Ihde, op. cit., p. 410.

years later by Arrhenius into the equation:

$$\frac{d \ln k}{d T} = \frac{E}{RT^2} ,$$

where E is the activation energy in kilocalories,
T is the absolute temperature in degrees Kelvin,
and R is the gas constant.

Integrating the above, one finds:

$$\ln k = \frac{-E}{RT} + \ln A ,$$

where lnA is the integration constant. Using common logarithms, the equation becomes:

$$\log k = \frac{-E}{2.303\ RT} + \log A$$

For any two rate constants at different temperatures of a reaction, the Arrhenius expression becomes:

$$\log (k_2/k_1) = \frac{E}{2.203\ R} \frac{T_2-T_1}{T_2T_1} .$$

which can be used to find the activation energy. The activation energy is the "additional energy the reactant molecules must acquire to form the activated complex for the reaction."[1]

By supposing that the equilibrium which exists between reacting molecules and the activated state decomposes at a definite rate, a rate expression can be derived for the specific rate of any reaction, namely:

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[1]Glasstone and Lewis, op. cit., p. 632.

$$k = \frac{RT}{Nh} K^* ,$$

where N is Avogadro's number,
h is Plank's constant,
and K* is the equilibrium constant between the activated state and the reactants.

From thermodynamics:

$$K^* = e^{S^*/R} \; e^{-E^*/RT} ,$$

where S* is the change in entropy of the system
and E* is the energy of activation for the activated complexes.

Substituting for K* in the above equation, one finds:

$$k = \frac{RT}{Nh} \; e^{S^*/R} \; e^{-E^*/RT}$$

which can be changed into the expression:

$$\log k = \frac{S^*}{2.303\ R} - \frac{E^*}{2.303\ RT} = \log \frac{RT}{Nh} ,$$

which may be solved for S* to determine the change in entropy for the system.[1]

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[1] Ibid., pp. 632-633.

TABLE II

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.0010 MOLES OF 1-CHLORO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.61	25.0	0.38[b]	0.68	1.057
0.91	33.0	0.33[b]	0.67	1.082
1.00	36.3	0.60	1.08	1.093
2.00	59.84	0.31	0.51	1.177
3.00	79.57	0.31	0.49	1.259
4.00	96.61	0.28	0.33	1.338
5.00	111.4	0.49	0.53	1.415
6.00	124.8	0.40	0.75	1.494
7.00	136.6	0.38	0.72	1.571
10.00	166.1	0.41	0.59	1.803
12.00	181.9	0.36	0.72	1.958
15.00	200.9	0.27	0.45	2.184
17.00	212.2	0.39	0.78	2.344
20.00	226.1	0.44	0.82	2.578
25.00	244.2	0.50	0.63	2.961
30.00	259.0	0.55	1.12	3.372
60.00	305.0	0.05	0.06	5.923

[a] C_o = 5.95 micromhos

C_∞ = 365.8 micromhos

[b] These values are calculated from errors in time.

TABLE III

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.0020 MOLES OF 1-CHLORO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.36	50.0	0.71[b]	1.24	1.073
0.52	66.7	0.66[b]	1.19	1.106
1.00	108.6	0.10	0.18	1.196
2.00	174.2	0.30	0.53	1.372
3.00	224.1	0.09	0.24	1.555
4.00	261.8	0.66	1.53	1.708
5.00	293.8	0.50	0.63	1.875
7.00	342.4	0.68	1.24	2.200
10.00	393.3	0.80	1.41	2.698
12.00	418.3	0.82	1.59	3.032
15.00	447.0	0.82	1.65	3.535
17.00	462.3	0.88	1.77	3.878
20.00	481.9	0.92	1.83	4.428
25.00	504.4	0.81	1.65	5.289
30.00	521.5	0.84	1.71	6.206

[a] C_o = 8.20 micromhos

C_∞ = 620.1 micromhos

[b] These values are calculated from errors in time.

TABLE IV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.0025 MOLES OF 1-CHLORO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.27	60.0	0.0 [b]	0.0	1.079
0.40	80.0	0.88 [b]	1.62	1.112
0.80	130.0	0.0 [b]	0.0	1.204
1.00	152.7	1.53	2.75	1.251
2.00	239.7	1.14	2.45	1.474
3.00	302.8	1.61	3.81	1.691
4.00	352.4	1.91	3.90	1.951
5.00	389.0	2.20	5.09	2.117
6.00	420.5	2.47	5.83	2.332
7.00	446.3	2.46	5.95	2.544
10.00	502.4	2.97	7.10	3.182
12.00	528.4	4.88	9.95	3.575
15.00	559.4	3.47	8.14	4.221
17.00	576.4	3.50	8.22	4.685
20.00	594.9	4.32	10.00	5.323
25.00	617.6	4.47	10.40	6.389
30.00	638.3	3.94	8.04	7.817
60.00	683.9	5.33	10.62	15.737

[a] C_o = 7.32 micromhos

C_∞ = 730.9 micromhos

[b] These values are calculated from errors in time.

TABLE V

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.0010 MOLES OF 1-CHLORO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.30	333.0	4.2[b]	8.5	1.050
0.53	500.0	3.6[b]	7.3	1.083
1.00	790.6	9.2	16.7	1.146
2.00	1,271	13.3	26.2	1.269
3.00	1,657	17.2	33.6	1.389
4.00	1,976	22.6	41.8	1.507
5.00	2,247	22.6	40.0	1.623
6.00	2,468	24.0	41.2	1.733
7.00	2,676	22.3	39.5	1.850
10.00	3,144	24.5	46.3	2.183
12.00	3,363	18.1	37.1	2.383
15.00	3,665	24.0	47.2	2.732
17.00	3,818	23.6	47.2	2.946
20.00	4,016	21.2	39.5	3.282
25.00	4,268	29.0	48.9	3.842
30.00	4,444	24.4	44.2	4.361
60.00	4,999	31.3	55.8	7.596

[a] C_o = 64.9 micromhos

C_∞ = 5,747 micromhos

[b] These values are calculated from errors in time.

TABLE VI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.0020 MOLES OF 1-CHLORO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.42	1,250	0.0[b]	0.0	1.135
0.52	1,428	0.0[b]	0.0	1.160
0.62	1,666	11.7[b]	21.1	1.195
1.00	2,291	11.1	22.3	1.297
2.00	3,558	0.0	0.0	1.569
3.00	4,412	12.8	26.1	1.827
4.00	5,061	22.2	45.3	2.089
5.00	5,568	19.7	40.2	2.352
7.00	5,948	18.8	38.4	2.598
10.00	6,273	20.2	41.2	2.850
12.00	6,964	20.7	42.2	3.598
15.00	7,290	21.9	44.6	4.106
17.00	7,665	20.0	36.0	4.902
20.00	7,837	36.6	65.6	5.381
25.00	8,060	20.3	41.4	6.193
30.00	8,326	18.3	37.3	7.450
60.00	9,073	17.3	31.2	18.050

[a] C_o = 122 micromhos

C_∞ = 9,598 micromhos

[b] These values are calculated from errors in time.

TABLE VII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.0025 MOLES OF 1-CHLORO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.20	1,000	17.2[b]	39.7	1.088
0.49	2,000	14.8[b]	30.2	1.207
0.88	3,000	0.0[b]	0.0	1.353
1.00	3,240	15.1	30.8	1.394
2.00	4,835	3.0	6.1	1.740
3.00	5,873	11.2	22.8	2.072
4.00	6,898	12.0	21.6	2.404
5.00	7,165	15.2	30.8	2.734
6.00	7,588	19.2	39.2	3.050
7.00	7,926	16.4	33.4	3.361
10.00	8,641	16.6	33.8	4.284
12.00	8,973	21.7	44.3	4.910
15.00	9,338	23.1	47.1	5.850
17.00	9,523	25.3	51.6	6.420
20.00	9,734	24.8	50.5	7.383
25.00	10,002	24.7	50.4	8.974
30.00	10,190	27.4	55.9	10.573
60.00	10,671	49.3	88.9	19.434

[a] C_o = 89.5 micromhos

C_∞ = 11,200 micromhos

[b] These values are calculated from errors in time.

TABLE VIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	2.85	0.14	0.29	1.003
1.00	2.96	0.15	0.25	1.004
3.00	3.41	0.16	0.28	1.007
5.00	3.82	0.16	0.34	1.009
7.00	4.24	0.16	0.36	1.012
10.00	4.86	0.17	0.39	1.016
15.00	5.87	0.22	0.44	1.022
20.00	6.92	0.30	0.53	1.029
25.00	7.92	0.33	0.62	1.035
30.00	8.86	0.37	1.13	1.042
60.00	14.54	0.38	0.70	1.081
90.00	19.63	0.52	1.03	1.118
120.00	24.50	0.58	1.13	1.157
180.00	36.24	0.18	0.36	1.261
240.00	44.88	0.19	0.36	1.351
300.00	52.33	0.17	0.34	1.439
420.00	63.88	0.22	0.50	1.602
600.00	78.79	0.27	0.52	1.875
720.00	85.97	0.24	0.48	2.043

[a] C_o = 2.31 micromhos

C_∞ = 166.2 micromhos

TABLE IX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	3.18	0.05	0.17	1.004
1.00	3.38	0.06	0.40	1.004
3.00	4.22	0.03	0.06	1.009
5.00	5.11	0.04	0.05	1.013
7.00	5.94	0.04	0.08	1.017
10.00	7.18	0.04	0.08	1.023
15.00	9.19	0.05	0.07	1.033
20.00	11.24	0.09	0.21	1.044
25.00	13.04	0.03	0.07	1.053
30.00	14.90	0.06	0.13	1.063
60.00	25.85	0.06	0.13	1.125
90.00	34.97	0.11	0.39	1.183
120.00	43.66	0.09	0.18	1.243
180.00	59.08	0.22	0.54	1.367
240.00	72.10	0.42	1.04	1.493
300.00	83.60	0.50	1.04	1.626
420.00	101.00	0.50	1.04	1.877
600.00	120.23	0.40	0.86	2.265
720.00	129.34	0.30	0.69	2.516

[a] C_o = 2.40 micromhos

C_∞ = 213.4 micromhos

TABLE X

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	3.32	0.13	0.27	1.002
1.00	3.69	0.13	0.28	1.003
3.00	5.28	0.10	0.34	1.009
5.00	6.76	0.19	0.41	1.015
7.00	8.19	0.20	0.40	1.020
10.00	10.37	0.21	0.44	1.029
15.00	13.77	0.25	0.53	1.042
20.00	17.10	0.26	0.57	1.056
25.00	19.97	0.07	0.12	1.067
30.00	23.43	0.32	0.67	1.082
60.00	40.68	0.32	0.68	1.162
90.00	55.35	0.45	0.99	1.240
120.00	70.50	0.22	0.50	1.333
180.00	92.51	0.46	1.01	1.494
240.00	110.63	0.22	0.50	1.661
300.00	124.79	0.30	0.64	1.819
420.00	147.69	0.17	0.37	2.149
600.00	171.49	0.46	1.01	2.650
720.00	183.95	0.69	1.56	3.017

[a] C_o = 2.85 micromhos

C_∞ = 273.72 micromhos

TABLE XI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.35	6.0	0.08[b]	0.12	1.007
0.67	7.0	0.09[b]	0.18	1.011
1.00	8.23	0.36	0.78	1.016
2.00	10.96	0.36	0.83	1.026
3.00	13.59	0.36	0.82	1.036
4.00	16.16	0.36	0.82	1.046
5.00	18.64	0.36	0.80	1.056
6.00	21.10	0.32	0.76	1.066
7.00	23.48	0.35	0.81	1.075
10.00	30.30	0.34	0.80	1.104
12.00	34.70	0.34	0.80	1.124
15.00	40.88	0.40	0.94	1.153
17.00	44.78	0.38	0.92	1.172
20.00	50.50	0.38	0.93	1.201
25.00	59.40	0.32	0.79	1.248
30.00	67.55	0.34	0.83	1.296
60.00	106.0	0.34	0.83	1.578
120.00	152.8	0.40	0.93	2.146

[a] C_o = 3.94 micromhos

C_∞ = 282.7 micromhos

[b] These values are calculated from errors in time.

TABLE XII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.42	8.0	0.23[b]	0.49	1.008
0.77	10.0	0.20[b]	0.43	1.013
1.00	11.0	0.12	0.29	1.016
2.00	16.47	0.22	0.49	1.031
3.00	21.38	0.21	0.47	1.045
4.00	26.10	0.21	0.49	1.059
5.00	30.61	0.21	0.48	1.073
6.00	35.05	0.22	0.49	1.086
7.00	39.59	0.09	0.16	1.101
10.00	51.76	0.04	0.09	1.141
12.00	57.50	0.01	0.03	1.161
15.00	69.91	0.08	0.14	1.208
17.00	76.55	0.01	0.03	1.234
20.00	86.00	0.08	0.13	1.273
25.00	100.3	0.09	0.18	1.338
30.00	113.2	0.15	0.29	1.399
60.00	162.6	1.00	1.71	1.717
120.00	224.1	4.19	9.92	2.385

[a] C_o = 5.08 micromhos

C_∞ = 382.2 micromhos

[b] These values are calculated from errors in time.

TABLE XIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.27	12.0	0.01[b]	0.02	1.012
0.68	16.0	0.02[b]	0.04	1.021
1.00	18.9	0.09	0.24	1.028
2.00	27.3	0.12	0.24	1.046
3.00	35.53	0.14	0.33	1.066
4.00	43.55	0.13	0.25	1.085
5.00	50.78	0.24	0.59	1.103
6.00	57.96	0.46	0.96	1.121
7.00	64.62	0.31	0.73	1.139
10.00	83.56	0.44	0.99	1.192
12.00	95.13	0.49	1.08	1.228
15.00	110.8	0.64	1.42	1.299
17.00	121.0	0.72	1.47	1.314
20.00	134.8	0.72	1.47	1.366
25.00	155.1	0.74	1.91	1.449
30.00	172.4	0.07	0.09	1.529
60.00	250.8	1.25	2.40	2.037

[a] C_o = 5.95 micromhos

C_∞ = 487.0 micromhos

[b] These values are calculated from errors in time.

TABLE XIV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.45	10.0	0.48[b]	1.03	1.014
0.68	12.0	0.32[b]	0.68	1.020
0.92	14.0	0.13[b]	0.27	1.026
1.00	14.4	0.15	0.39	1.027
1.50	18.64	0.44	0.99	1.041
2.00	22.39	0.37	0.82	1.052
2.50	26.15	0.48	1.10	1.064
3.00	29.89	0.60	1.37	1.077
3.50	33.43	0.62	1.34	1.089
4.00	36.93	0.76	1.69	1.101
4.50	40.25	0.82	1.83	1.113
5.00	43.53	0.90	1.98	1.124
7.00	55.81	1.22	2.70	1.171
10.00	71.42	1.79	3.72	1.236
15.00	95.02	2.50	4.92	1.350
20.00	114.5	3.12	5.83	1.460
30.00	147.1	4.68	9.57	1.692
60.00	210.1	3.34	8.36	2.443
90.00	242.8	3.37	8.46	3.173

[a] C_o = 5.12 micromhos

C_∞ = 352.2 micromhos

[b] These values are calculated from errors in time.

TABLE XV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.32	13.0	0.05[b]	0.10	1.016
0.42	15.0	0.17[b]	0.36	1.020
0.68	20.0	0.15[b]	0.32	1.031
1.00	25.7	0.18	0.24	1.044
1.50	34.3	0.26	0.59	1.064
2.00	42.39	0.30	0.59	1.083
2.50	50.24	0.36	0.75	1.103
3.00	57.71	0.32	0.65	1.122
3.50	65.03	0.37	0.65	1.142
4.00	71.96	0.36	0.73	1.161
4.50	78.69	0.42	0.75	1.180
5.00	95.09	0.42	0.79	1.199
7.00	108.8	0.48	0.78	1.274
10.00	139.0	0.60	0.88	1.385
15.00	179.4	0.66	1.13	1.567
20.00	211.1	0.74	1.32	1.748
30.00	258.5	0.46	0.88	2.112
60.00	337.4	1.13	2.39	3.233
90.00	375.3	0.90	1.81	4.339

[a] C_o = 5.39 micromhos

C_∞ = 486.1 micromhos

[b] These values are calculated from errors in time.

TABLE XVI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 1 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.28	20.0	0.20[b]	0.42	1.023
0.43	25.0	0.16[b]	0.34	1.032
0.60	30.0	0.12[b]	0.25	1.041
1.00	42.5	0.20	0.44	1.064
1.50	56.8	0.08	0.19	1.091
2.00	70.2	0.14	0.29	1.118
2.50	82.9	0.16	0.34	1.145
3.00	94.9	0.22	0.49	1.171
3.50	106.4	0.34	0.73	1.198
4.00	117.1	0.38	0.78	1.224
4.50	127.4	0.45	0.98	1.250
5.00	137.2	0.48	1.08	1.276
7.00	172.5	0.77	1.57	1.378
10.00	216.2	0.86	1.91	1.530
15.00	272.0	1.07	2.26	1.782
20.00	313.7	1.18	2.50	2.216
30.00	373.7	1.35	2.85	2.532
60.00	465.3	1.44	3.29	4.133
90.00	504.7	2.13	3.95	5.654

[a] C_o = 6.36 micromhos
C_∞ = 611.8 micromhos

[b] These values are calculated from errors in time.

TABLE XVII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	42.5	2.10	4.51	1.002
1.00	44.4	3.10	7.05	1.003
3.00	54.25	3.02	6.55	1.007
5.00	63.92	2.88	6.10	1.011
7.00	73.41	2.68	5.92	1.015
10.00	87.58	2.72	6.29	1.020
15.00	109.6	3.04	6.52	1.030
20.00	131.1	3.44	7.10	1.039
25.00	154.6	2.66	5.44	1.049
30.00	175.2	2.94	5.20	1.058
60.00	288.0	4.40	9.60	1.111
90.00	394.5	6.56	12.31	1.167
120.00	486.6	10.66	21.18	1.219
180.00	698.8	1.32	4.31	1.360
240.00	851.9	2.60	4.13	1.483
300.00	988.3	3.25	6.74	1.614
420.00	1,186.1	2.82	3.20	1.850
600.00	1,403.8	1.86	3.78	2.206
720.00	1,514.7	3.14	7.08	2.444

[a] C_o = 37.50 micromhos

C_∞ = 2,536.6 micromhos

TABLE XVIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	44.20	0.45	0.90	1.003
1.00	49.66	0.58	1.18	1.005
3.00	69.16	0.89	1.03	1.010
5.00	87.53	0.73	1.36	1.016
7.00	106.7	0.74	1.56	1.022
10.00	134.0	0.82	1.86	1.031
15.00	178.1	0.87	2.01	1.045
20.00	220.5	1.09	2.25	1.059
25.00	261.2	1.12	2.40	1.073
30.00	302.3	0.25	1.06	1.088
60.00	521.0	3.56	6.20	1.172
90.00	703.2	3.38	7.34	1.253
120.00	886.5	2.82	5.00	1.346
180.00	1,165.6	3.66	8.00	1.518
240.00	1,394.0	2.70	4.65	1.697
300.00	1,570.2	6.74	14.16	1.827
420.00	1,849.0	6.36	14.04	2.210
600.00	2,144.2	3.82	15.67	2.752
720.00	2,278.0	6.70	14.69	3.096

[a] C_o = 34.77 micromhos

C_∞ = 3,348 micromhos

TABLE XIX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	55.26	0.80	1.68	1.003
1.00	64.08	0.74	1.45	1.005
3.00	98.53	1.10	2.47	1.013
5.00	131.6	1.32	2.95	1.022
7.00	164.1	1.42	3.28	1.030
10.00	210.9	1.70	3.73	1.042
15.00	285.7	1.95	4.23	1.062
20.00	356.4	1.98	5.38	1.082
25.00	424.0	2.82	5.96	1.101
30.00	488.6	3.20	6.65	1.120
60.00	838.6	7.71	5.20	1.237
90.00	1,113.8	8.00	17.08	1.348
120.00	1,401.9	2.08	4.64	1.488
180.00	1,788.3	3.66	3.66	1.727
240.00	2,079.6	5.72	12.00	1.966
300.00	2,299.4	11.90	22.76	2.195
420.00	2,609.7	8.89	22.47	2.628
600.00	2,989.0	14.30	28.70	3.460
720.00	3,187.6	16.40	35.43	4.149

[a] C_o = 44.17 micromhos

C_∞ = 4,186 micromhos

TABLE XX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.32	90.0	4.9[b]	10.0	1.008
0.45	100.0	3.0[b]	6.12	1.010
1.00	140.0	14.5	17.1	1.020
2.00	200.5	7.2	17.1	1.035
3.00	257.8	7.4	17.1	1.050
4.00	318.4	7.1	13.6	1.067
5.00	360.8	11.2	26.2	1.078
6.00	416.9	7.0	16.3	1.094
7.00	466.6	6.6	15.3	1.109
10.00	606.6	6.7	15.3	1.152
12.00	693.7	7.2	16.0	1.180
15.00	815.8	7.0	14.9	1.222
17.00	891.8	7.2	15.3	1.250
20.00	999.6	7.0	14.9	1.291
25.00	1,164	7.2	15.2	1.361
30.00	1,312	6.6	15.2	1.431
60.00	1,968	6.7	14.7	1.847
120.00	2,676	8.2	18.6	2.693

[a] C_o = 58.65 micromhos

C_∞ = 4,222 micromhos

[b] These values are calculated from errors in time.

TABLE XXI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.53	150.0	3.0[b]	6.4	1.014
0.80	180.0	3.0[b]	6.4	1.020
1.00	206.0	2.5	5.4	1.024
2.00	318.0	3.3	5.8	1.045
3.00	423.6	3.4	7.4	1.066
4.00	523.9	2.6	5.1	1.087
5.00	620.3	3.4	7.6	1.107
6.00	712.5	3.0	7.1	1.127
7.00	798.3	3.4	7.8	1.147
10.00	1,039	3.4	8.3	1.206
12.00	1,185	4.3	10.3	1.244
15.00	1,387	4.4	10.3	1.302
17.00	1,508	4.8	10.7	1.339
20.00	1,680	5.2	11.2	1.396
25.00	1,936	5.5	12.2	1.490
30.00	2,159	6.5	14.7	1.582
60.00	3,083	9.8	19.6	2.132

[a] C_o = 71.43 micromhos

C_∞ = 5,944 micromhos

[b] These values are calculated from errors in time.

TABLE XXII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.37	200.0	0.9[b]	1.8	1.017
0.60	250.0	0.8[b]	1.6	1.024
1.00	329.0	1.2	5.9	1.036
2.00	519.0	1.6	3.9	1.065
3.00	695.0	1.9	4.4	1.094
4.00	861.0	1.6	3.0	1.122
5.00	1,014	2.3	4.9	1.150
6.00	1,160	2.0	4.4	1.177
7.00	1,297	2.0	4.4	1.204
10.00	1,670	3.1	6.9	1.284
12.00	1,889	2.8	5.9	1.336
15.00	2,187	3.3	7.3	1.414
17.00	2,366	3.6	7.3	1.466
20.00	2,613	3.6	7.3	1.543
25.00	2,970	4.3	8.8	1.670
30.00	3,275	5.2	9.8	1.797
60.00	4,468	8.1	18.9	2.581

[a] C_o = 84.10 micromhos

C_∞ = 7,264 micromhos

[b] These values are calculated from errors in time.

TABLE XXIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.57	150.0	2.0[b]	8.7	1.013
0.65	200.0	3.0[b]	12.5	1.023
0.75	220.0	2.5[b]	10.5	1.027
1.00	276.0	4.8	10.3	1.038
1.50	359.0	2.4	5.4	1.055
2.00	445.0	2.8	6.8	1.074
2.50	527.0	1.4	3.3	1.092
3.00	607.9	2.1	5.1	1.108
3.50	684.6	2.2	4.6	1.129
4.00	757.4	1.8	2.8	1.147
4.50	829.4	1.6	3.9	1.165
5.00	899.4	1.4	3.3	1.183
7.00	1,151	1.2	4.4	1.254
10.00	1,477	1.2	2.9	1.359
15.00	1,915	1.1	2.4	1.532
20.00	1,702	0.8	1.9	1.702
30.00	2,772	2.8	5.9	2.039
60.00	3,644	2.2	4.4	3.094
90.00	4,078	2.1	4.9	4.114

[a] C_o = 82.39 micromhos

C_∞ = 5,361 micromhos

[b] These values are calculated from errors in time.

TABLE XXIV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.30	220.0	0.0[b]	0.0	1.020
0.48	300.0	0.0[b]	0.0	1.031
0.62	350.0	0.0[b]	0.0	1.039
1.00	501.0	3.1	7.4	1.062
1.50	684.0	4.1	9.3	1.091
2.00	858.0	4.7	10.8	1.120
2.50	1,021	5.0	10.8	1.149
3.00	1,172	3.9	9.7	1.178
3.50	1,317	5.2	12.2	1.206
4.00	1,454	4.8	11.3	1.234
4.50	1,582	4.8	10.7	1.262
5.00	1,706	5.2	12.2	1.290
7.00	2,148	4.9	11.7	1.400
10.00	2,689	6.2	13.7	1.563
15.00	3,370	6.8	13.3	1.833
20.00	3,874	6.8	12.7	2.100
30.00	4,579	8.0	13.7	2.640
60.00	5,666	14.0	20.5	4.372
90.00	6,152	10.3	19.5	6.186

[a] C_o = 79.00 micromhos

C_∞ = 7,323 micromhos

[b] These values are calculated from errors in time.

TABLE XXV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-IODO-2,4-DINITROBENZENE IN CELL 2 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.32	400.0	2.2[b]	4.7	1.034
0.48	500.0	2.8[b]	6.0	1.046
0.73	700.0	2.4[b]	5.1	1.071
1.00	838.0	1.4	2.9	1.088
1.50	1,132	2.5	5.7	1.128
2.00	1,403	6.5	10.8	1.151
2.50	1,656	5.9	12.7	1.206
3.00	1,883	6.6	13.7	1.243
3.50	2,102	7.5	15.2	1.282
4.00	2,303	8.4	17.6	1.319
4.50	2,494	9.8	20.1	1.356
5.00	2,674	9.8	20.6	1.394
7.00	3,304	11.1	22.0	1.542
10.00	4,042	12.3	24.0	1.762
15.00	4,929	15.6	28.9	2.126
20.00	5,557	14.7	28.9	2.491
30.00	6,396	15.2	30.4	3.231
60.00	7,606	8.7	21.8	5.653
90.00	8,061	5.5	13.0	7.872

[a] C_o = 98.54 micromhos

C_∞ = 9,220 micromhos

[b] These values are calculated from errors in time.

TABLE XXVI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	2.66	0.09	0.21	1.003
1.00	3.06	0.15	0.29	1.005
2.00	3.62	0.11	0.56	1.010
3.00	5.08	0.08	0.17	1.020
4.00	5.95	0.13	0.18	1.027
5.00	6.87	0.08	0.16	1.038
7.00	8.63	0.07	0.16	1.048
10.00	11.06	0.11	0.27	1.068
15.00	15.00	0.09	0.29	1.101
20.00	18.71	0.06	0.14	1.135
25.00	22.13	0.08	0.19	1.167
30.00	25.33	0.08	0.17	1.200
60.00	41.54	0.21	0.44	1.357
90.00	53.66	0.26	0.57	1.591
120.00	63.18	0.18	0.41	1.787
150.00	70.61	0.26	0.62	1.978

[a] C_o = 2.31 micromhos

C_∞ = 140.48 micromhos

TABLE XXVII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	3.66	0.04	0.09	1.007
1.00	4.71	0.04	0.07	1.012
2.00	6.77	0.06	0.15	1.023
3.00	8.79	0.06	0.13	1.034
4.00	10.74	0.06	0.15	1.074
5.00	12.63	0.06	0.12	1.056
7.00	12.26	0.05	0.11	1.078
10.00	21.34	0.05	0.11	1.109
15.00	29.11	0.07	0.16	1.161
20.00	36.11	0.08	0.17	1.212
25.00	42.46	0.09	0.21	1.263
30.00	48.34	0.10	0.28	1.314
60.00	75.62	0.13	0.29	1.614
90.00	94.45	0.28	0.60	1.917
120.00	108.55	0.27	0.53	2.230
150.00	119.22	0.27	0.57	2.545

[a] C_o = 2.40 micromhos

C_∞ = 194.85 micromhos

TABLE XXVIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	4.98	0.02	0.04	1.009
1.00	6.84	0.06	0.18	1.017
2.00	10.40	0.06	0.16	1.032
3.00	13.84	0.05	0.14	1.047
4.00	17.18	0.06	0.15	1.062
5.00	20.34	0.03	0.08	1.077
7.00	26.35	0.04	0.09	1.106
10.00	34.63	0.04	0.09	1.149
15.00	46.96	0.04	0.08	1.218
20.00	57.76	0.06	0.14	1.289
25.00	67.28	0.06	0.15	1.357
30.00	75.87	0.03	0.09	1.425
60.00	114.2	0.21	0.54	1.835
90.00	138.7	0.02	0.05	2.247
120.00	155.6	0.06	0.09	2.660
150.00	168.2	0.07	0.14	3.082

[a] C_o = 2.85 micromhos

C_∞ = 247.6 micromhos

TABLE XXIX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.53	9.00	0.08[b]	0.17	1.021
0.85	12.00	0.20[b]	0.43	1.035
1.00	13.31	0.04	0.19	1.041
2.00	21.84	0.10	0.23	1.081
3.00	29.69	0.10	0.23	1.121
4.00	36.90	0.12	0.24	1.160
5.00	43.56	0.14	0.31	1.200
7.00	55.50	0.18	0.39	1.276
10.00	70.84	0.23	0.54	1.390
12.00	79.57	0.24	0.53	1.465
15.00	91.32	0.16	0.38	1.579
20.00	107.10	0.24	0.48	1.763
25.00	119.58	0.38	0.72	1.942
30.00	130.52	0.34	0.73	2.132
60.00	168.65	0.24	0.53	3.235
90.00	187.97	0.47	0.87	4.385
120.00	199.20	0.51	0.95	5.504

[a] C_o = 5.12 micromhos

C_∞ = 242.33 micromhos

[b] These values are calculated from errors in time.

TABLE XXX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.25	10.00	0.18[b]	0.38	1.012
0.48	15.00	0.13[b]	0.28	1.028
1.00	25.20	0.08	0.18	1.062
2.00	42.64	0.12	0.23	1.126
3.00	57.73	0.19	0.37	1.188
4.00	71.11	0.26	0.46	1.248
5.00	83.10	0.30	0.58	1.308
7.00	103.90	0.36	0.75	1.426
10.00	129.14	0.38	0.79	1.602
12.00	142.93	0.52	0.97	1.718
15.00	160.22	0.59	1.21	1.891
20.00	183.36	0.64	1.19	2.177
25.00	200.90	0.67	1.22	2.470
30.00	214.72	0.62	1.11	2.758
60.00	261.20	1.08	2.19	4.534
90.00	282.42	1.33	3.10	6.421
120.00	293.78	1.48	3.15	8.261

[a] C_o = 5.08 micromhos

C_∞ = 333.4 micromhos

[b] Theses values are calculated from errors in time.

TABLE XXXI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.25	15.0	0.16[b]	0.34	1.022
0.67	30.0	0.0 [b]	0.0	1.062
1.00	40.6	0.05	0.18	1.064
2.00	68.1	0.16	0.23	1.178
3.00	91.4	0.16	0.37	1.263
4.00	111.4	0.22	0.47	1.346
5.00	129.0	0.28	0.58	1.428
7.00	158.3	0.32	0.66	1.590
10.00	192.4	0.42	0.79	1.832
12.00	210.4	0.44	0.97	1.992
15.00	232.5	0.49	1.21	2.231
20.00	260.5	0.59	1.20	2.631
25.00	281.3	0.65	1.22	3.035
30.00	297.3	0.70	1.10	3.442
60.00	347.9	1.04	2.18	5.911
90.00	369.0	2.22	3.09	8.635
120.00	380.9	2.24	3.14	11.853

[a] C_o = 5.95 micromhos

C_∞ = 416.5 micromhos

[b] These values are calculated from errors in time.

TABLE XXXII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.48	20.0	0.16[b]	0.34	1.051
0.65	25.0	0.16[b]	0.34	1.069
0.82	30.00	0.0 [b]	0.0	1.088
1.00	34.64	0.06	0.13	1.107
1.50	47.14	0.08	0.20	1.159
2.00	58.03	0.08	0.19	1.208
2.50	68.67	0.08	0.19	1.261
3.00	77.75	0.09	0.20	1.310
3.50	86.36	0.12	0.25	1.360
4.00	94.34	0.18	0.39	1.410
4.50	101.62	0.21	0.48	1.459
5.00	108.7	0.28	0.59	1.510
7.00	131.9	0.31	0.74	1.705
10.00	158.4	0.42	0.98	1.999
15.00	188.5	0.45	1.03	2.487
20.00	208.8	0.46	1.03	2.977
30.00	234.6	0.56	1.32	3.973

[a] C_o = 5.12 micromhos
C_∞ = 311.8 micromhos

[b] These values are calculated from errors in time.

TABLE XXXIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.20	20.0	0.0 [b]	0.0	1.036
0.34	30.0	0.07 [b]	0.13	1.062
0.68	50.0	0.35 [b]	0.75	1.119
1.00	66.5	0.17	0.29	1.170
1.50	89.5	0.37	0.58	1.251
2.00	119.4	0.28	0.48	1.330
2.50	126.3	0.36	0.55	1.405
3.00	142.3	0.30	0.44	1.484
3.50	156.3	0.26	0.44	1.562
4.00	168.7	0.24	0.54	1.637
4.50	180.3	0.25	0.62	1.715
5.00	190.6	0.35	0.81	1.790
7.00	225.0	0.22	0.49	2.098
10.00	261.0	0.20	0.44	2.559
15.00	299.2	0.15	0.29	3.336
20.00	323.4	0.12	0.29	4.130
30.00	352.2	0.13	0.29	5.764

[a] C_o = 5.39 micromhos
C_∞ = 425.0 micromhos

[b] These values are calculated from errors in time.

TABLE XXXIV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 1 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.18	30.0	0.13[b]	0.28	1.047
0.37	50.0	0.13[b]	0.28	1.089
0.67	80.0	0.36[b]	0.74	1.161
1.00	107.2	0.30	0.34	1.234
1.50	142.9	0.35	0.83	1.346
2.00	171.4	0.50	0.64	1.450
2.50	196.1	0.61	1.07	1.555
3.00	217.8	0.60	1.32	1.666
3.50	237.2	0.50	1.03	1.767
4.00	254.1	0.58	1.12	1.872
4.50	269.0	0.44	0.94	1.976
5.00	282.6	0.62	1.32	2.081
7.00	325.3	0.56	1.22	2.499
10.00	368.1	0.62	1.42	3.128
15.00	411.0	0.68	1.52	4.184
20.00	437.0	0.52	1.22	5.260
30.00	467.3	0.67	1.56	7.478

[a] C_o = 6.36 micromhos
C_∞ = 538.1 micromhos

[b] These values are calculated from errors in time.

TABLE XXXV

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	43.9	0.57	1.2	1.003
1.00	52.4	0.84	1.5	1.007
2.00	74.66	0.47	0.9	1.018
3.00	97.70	1.00	3.4	1.029
4.00	118.8	1.56	3.4	1.040
5.00	138.8	2.40	5.3	1.050
7.00	173.7	2.35	3.4	1.068
10.00	230.1	1.87	4.2	1.099
15.00	304.1	2.45	5.4	1.143
20.00	373.6	3.84	9.2	1.188
25.00	446.4	2.86	5.4	1.238
30.00	506.1	3.82	6.1	1.283
60.00	810.4	4.8	8.8	1.571
90.00	1,020	1.14	2.0	1.859
120.00	1,168	2.74	5.9	2.175
150.00	1,286	2.28	3.9	2.422

[a] C_o = 37.50 micromhos

C_∞ = 2,164 micromhos

TABLE XXXVI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	64.8	0.78	1.6	1.010
1.00	89.5	0.80	1.8	1.019
2.00	138.0	0.90	1.5	1.036
3.00	182.3	0.64	1.5	1.052
4.00	225.4	0.56	1.3	1.069
5.00	267.4	1.13	2.5	1.085
7.00	344.2	1.10	2.6	1.116
10.00	449.7	0.86	2.2	1.163
15.00	606.7	0.76	2.9	1.240
20.00	743.3	1.93	3.9	1.315
25.00	861.7	1.50	3.4	1.388
30.00	968.3	2.06	4.6	1.461
60.00	1,440	2.06	4.9	1.905
90.00	1,735	2.34	4.9	2.352
120.00	1,940	2.96	6.9	2.810
150.00	2,090	3.20	6.9	3.277

[a] C_o = 34.77 micromhos

C_∞ = 2,992 micromhos

TABLE XXXVII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 0.1° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.50	92.4	0.16	0.35	1.013
1.00	135.6	0.80	1.9	1.026
2.00	217.0	0.80	1.9	1.050
3.00	293.0	1.24	2.3	1.073
4.00	364.3	1.30	2.9	1.095
5.00	431.6	1.28	2.7	1.117
7.00	556.5	1.51	3.4	1.161
10.00	722.4	1.90	5.3	1.224
15.00	859.8	2.30	5.5	1.327
20.00	1,160	3.60	7.8	1.429
25.00	1,331	2.88	6.8	1.529
30.00	1,482	3.28	7.8	1.629
60.00	2,106	2.65	5.4	2.239
90.00	2,469	3.35	6.9	2.861
120.00	2,708	3.56	7.8	3.502
150.00	2,876	4.87	9.1	4.157

[a] C_o = 44.17 micromhos

C_∞ = 3,779.5 micromhos

TABLE XXXVIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.20	100.0	0.0[b]	0.0	1.012
0.67	200.0	0.0[b]	0.0	1.041
1.00	266.2	0.42	0.88	1.062
2.00	447.2	0.43	0.93	1.122
3.00	601.5	1.18	1.82	1.182
4.00	742.6	0.92	2.10	1.237
5.00	867.7	0.88	1.91	1.293
7.00	1,084.4	0.62	0.98	1.403
10.00	1,344.6	0.28	0.65	1.563
12.00	1,488.0	0.61	1.47	1.668
15.00	1,668.7	0.59	1.27	1.821
20.00	1,905.5	0.54	1.27	2.071
25.00	2,086.1	0.72	1.48	2.314
30.00	2,229.4	0.71	1.18	2.551
60.00	2,709.1	0.58	1.37	3.881
90.00	2,923.6	0.80	1.91	5.060
120.00	3,045.0	1.60	3.37	6.112

[a] C_o = 58.65 micromhos

C_∞ = 6,273 micromhos

[b] These values are calculated from errors in time.

TABLE XXXIX

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.26	200.0	1.4[b]	3.0	1.027
0.69	400.0	1.2[b]	2.6	1.071
1.00	524.0	1.8	4.4	1.101
2.00	876.0	2.0	4.9	1.194
3.00	1,170	2.2	6.9	1.285
4.00	1,421	3.0	8.9	1.375
5.00	1,637	3.7	10.8	1.463
7.00	1,947	4.8	10.3	1.637
10.00	2,410	4.8	10.3	1.896
12.00	2,623	5.0	11.3	2.064
15.00	2,890	5.2	9.8	2.323
20.00	3,222	4.8	14.7	2.752
25.00	3,470	6.6	12.2	3.193
30.00	3,652	6.0	12.2	3.619
60.00	4,236	7.6	16.6	6.310
90.00	4,481	8.5	19.6	9.190
120.00	4,613	9.0	20.6	12.165

[a] C_o = 71.43 micromhos

C_∞ = 6,273 micromhos

[b] These values are calculated from errors in time.

TABLE XL

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 25.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.36	400.0	1.5[b]	3.2	1.054
0.64	600.0	1.4[b]	3.0	1.091
1.00	833.2	1.8	4.4	1.138
2.00	1,383.0	1.4	4.4	1.266
3.00	1,815.0	2.4	4.9	1.388
4.00	2,178.0	1.0	6.8	1.511
5.00	2,480	1.8	8.3	1.632
7.00	2,963	3.0	10.8	1.870
10.00	3,492	3.0	10.3	2.225
12.00	3,760	3.8	10.3	2.462
15.00	4,076	3.1	11.2	2.817
20.00	4,462	4.0	9.8	3.418
25.00	4,736	3.6	14.6	4.025
30.00	4,941	3.7	12.2	4.644
60.00	5,562	4.4	16.6	8.699
90.00	5,804	4.5	19.6	13.175
120.00	5,935	4.1	20.6	18.269

[a] C_o = 84.10 micromhos

C_∞ = 6,273 micromhos

[b] These values are calculated from errors in time.

TABLE XLI

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00050 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.23	250.0	0.07[b]	0.13	1.038
0.63	500.0	0.07[b]	0.13	1.100
0.80	600.0	0.09[b]	0.18	1.127
1.00	708.0	1.0	1.9	1.158
1.50	954.0	2.2	4.9	1.235
2.00	1,168	3.0	6.4	1.310
2.50	1,350	3.3	7.8	1.382
3.00	1,524	3.6	7.3	1.458
3.50	1,672	3.0	6.4	1.530
4.00	1,810	2.5	5.4	1.604
4.50	1,936	3.0	5.9	1.678
5.00	2,049	3.7	8.3	1.750
7.00	2,424	4.1	9.3	2.043
10.00	2,818	5.4	11.3	2.477
15.00	3,239	7.0	15.7	3.206
20.00	3,513	5.7	10.6	3.965
30.00	3,834	14.9	26.4	5.488

[a] C_o = 82.39 micromhos
C_∞ = 4,670 micromhos

[b] These values are calculated from errors in time.

TABLE XLII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00075 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.12	300.0	1.0[b]	2.1	1.037
0.27	500.0	0.0[b]	0.0	1.073
0.68	1,000	0.0[b]	0.0	1.176
1.00	1,312	4.6	10.3	1.250
1.50	1,748	4.4	9.8	1.371
2.00	2,102	3.8	7.3	1.488
2.50	2,406	4.4	9.8	1.606
3.00	2,669	3.8	9.2	1.724
3.50	2,900	5.1	10.3	1.843
4.00	3,105	4.8	9.6	1.964
4.50	3,285	4.8	10.3	2.083
5.00	3,442	5.6	10.3	2.200
7.00	3,947	4.3	8.8	2.683
10.00	4,449	4.8	10.8	3.433
15.00	4,947	4.6	10.3	4.750
20.00	5,252	3.1	6.5	6.209
30.00	5,587	5.0	11.3	9.371

[a] C_o = 79.00 micromhos
C_∞ = 6,245 micromhos

[b] These values are calculated from errors in time.

TABLE XLIII

AVERAGE CONDUCTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: 0.00100 MOLES OF 1-BROMO-2,4-DINITROBENZENE IN CELL 2 AT 40.0° C

Time in Minutes	Average C_t in micromhos	$\frac{s}{\sqrt{N}}$	95 per cent confidence interval	$\frac{C_\infty - C_o}{C_\infty - C_t}$ [a]
0.13	700.0	12.8[b]	27.2	1.081
0.20	1,000	11.0[b]	23.4	1.126
0.36	1,500	8.7[b]	18.5	1.211
1.00	2,124	16.1	38.6	1.337
1.50	2,739	7.3	15.0	1.490
2.00	3,233	10.1	20.6	1.640
2.50	3,655	10.0	24.1	1.795
3.00	3,991	9.2	21.5	1.941
3.50	4,288	9.0	21.9	2.091
4.00	4,540	12.3	29.6	2.238
4.50	4,769	12.7	30.5	2.390
5.00	4,966	7.0	16.3	2.539
7.00	5,557	9.8	22.3	3.122
10.00	6,102	11.9	24.1	3.962
15.00	6,648	13.1	30.3	5.422
20.00	6,931	32.2	62.5	6.703
30.00	7,292	12.1	25.0	9.594

[a] C_o = 98.54 micromhos; C_∞ = 8,129 micromhos

[b] These values are calculated from errors in time.

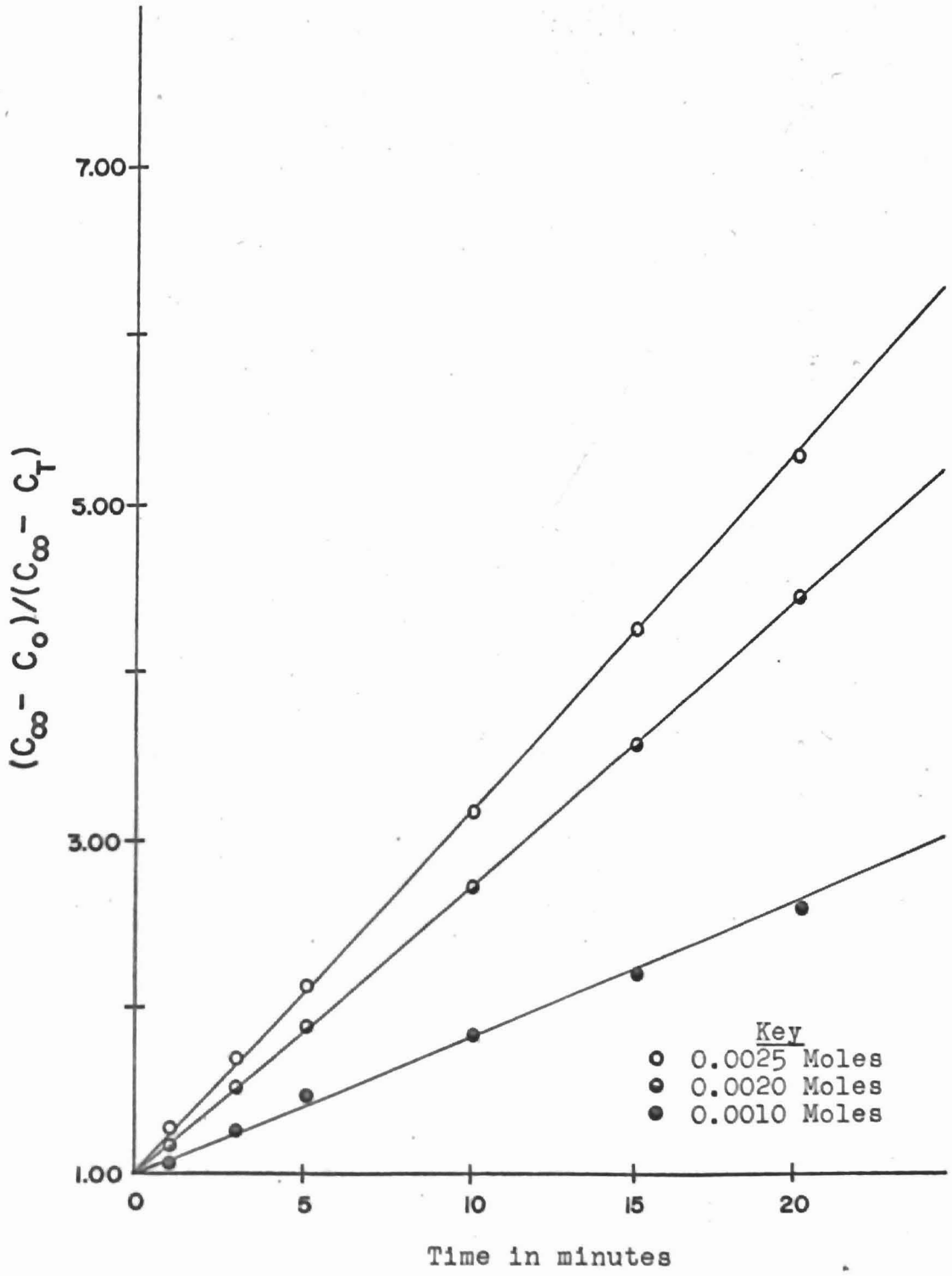

Figure 1. Increase in conductance ratio with time: 1-chloro-2,4-dinitrobenzene in cell 1 at 25.0° Centigrade.

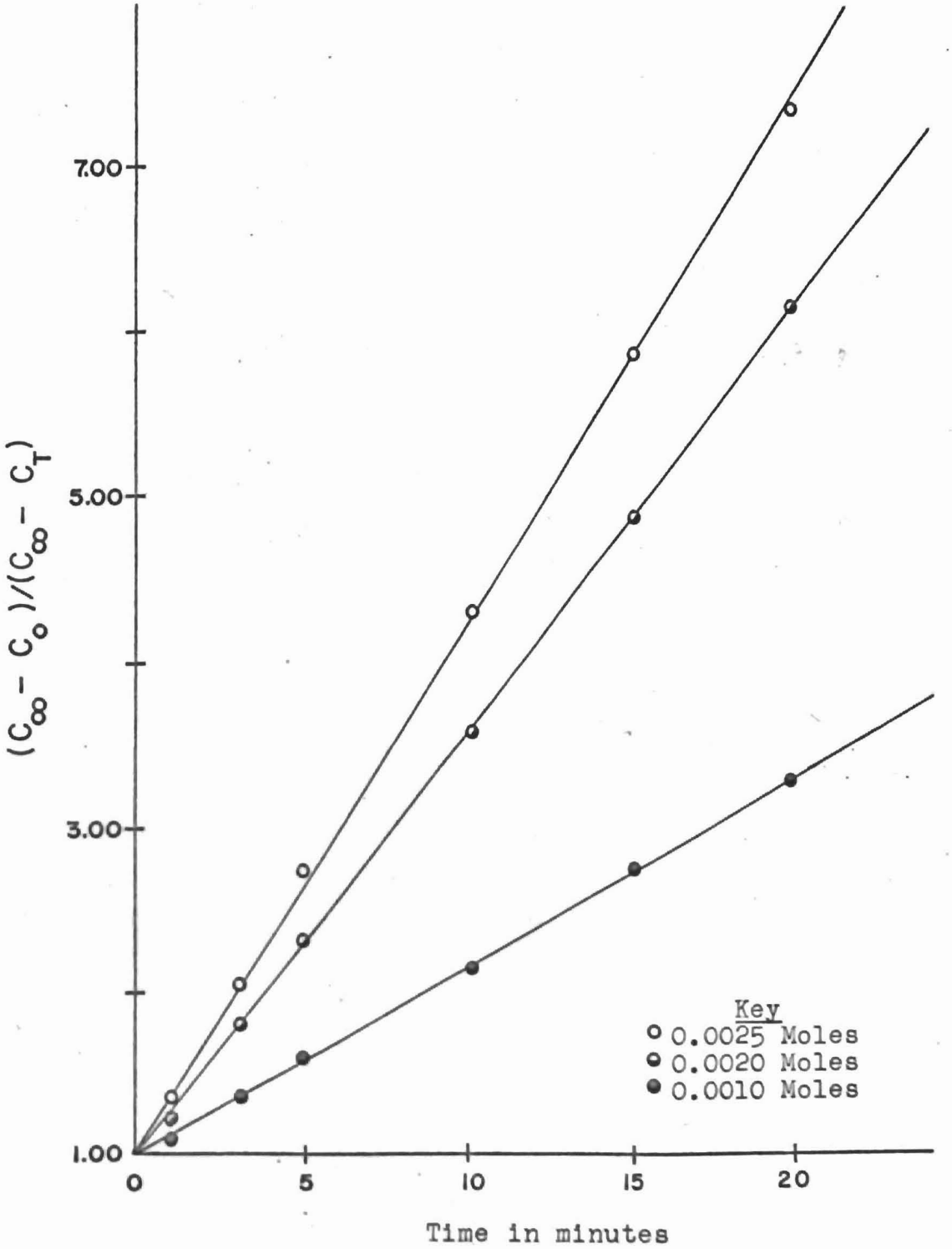

Figure 2. Increase in conductance ratio with time: 1-chloro-2,4-dinitrobenzene in cell 2 at 25.0° Centigrade.

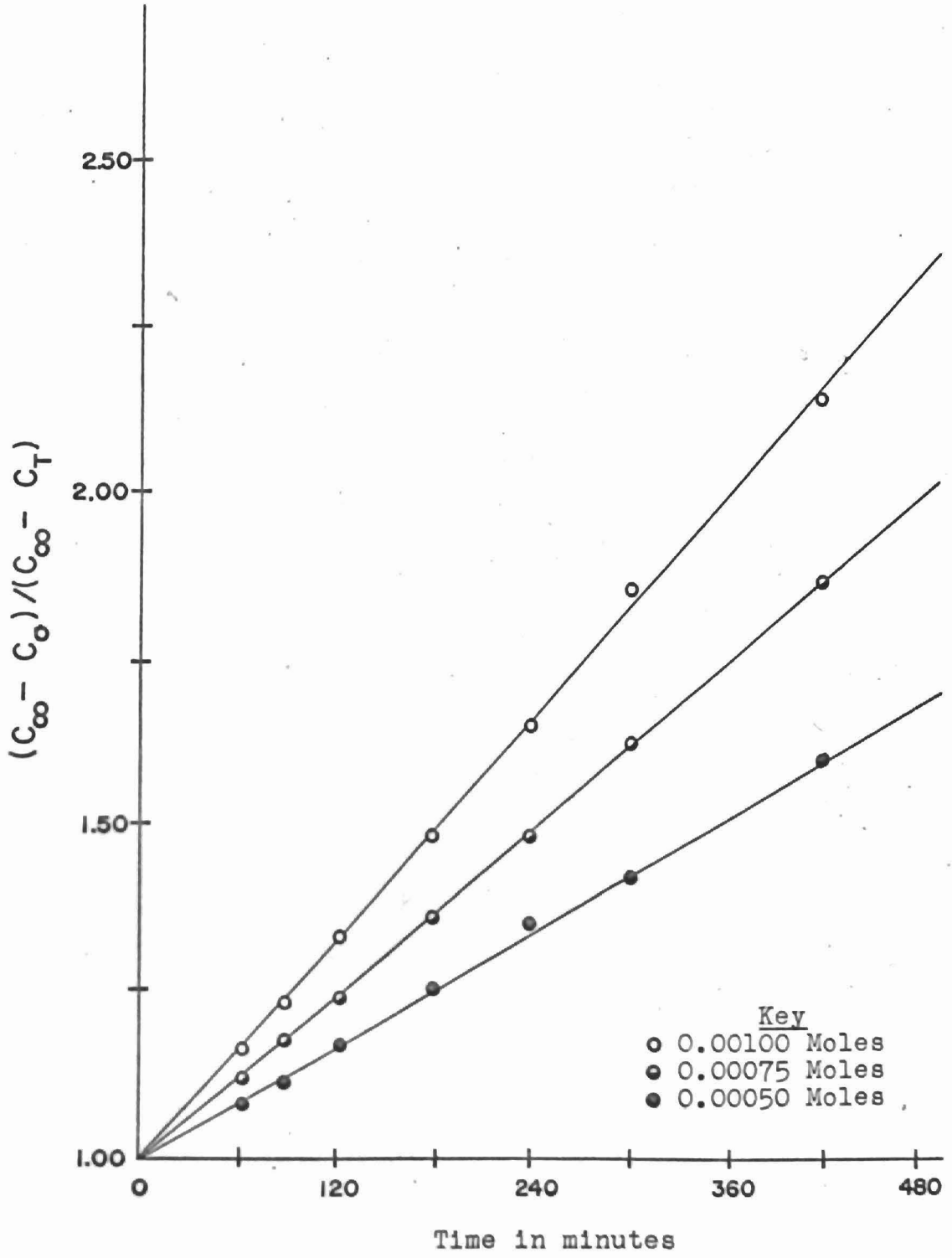

Figure 3. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 1 at 0.1° Centigrade.

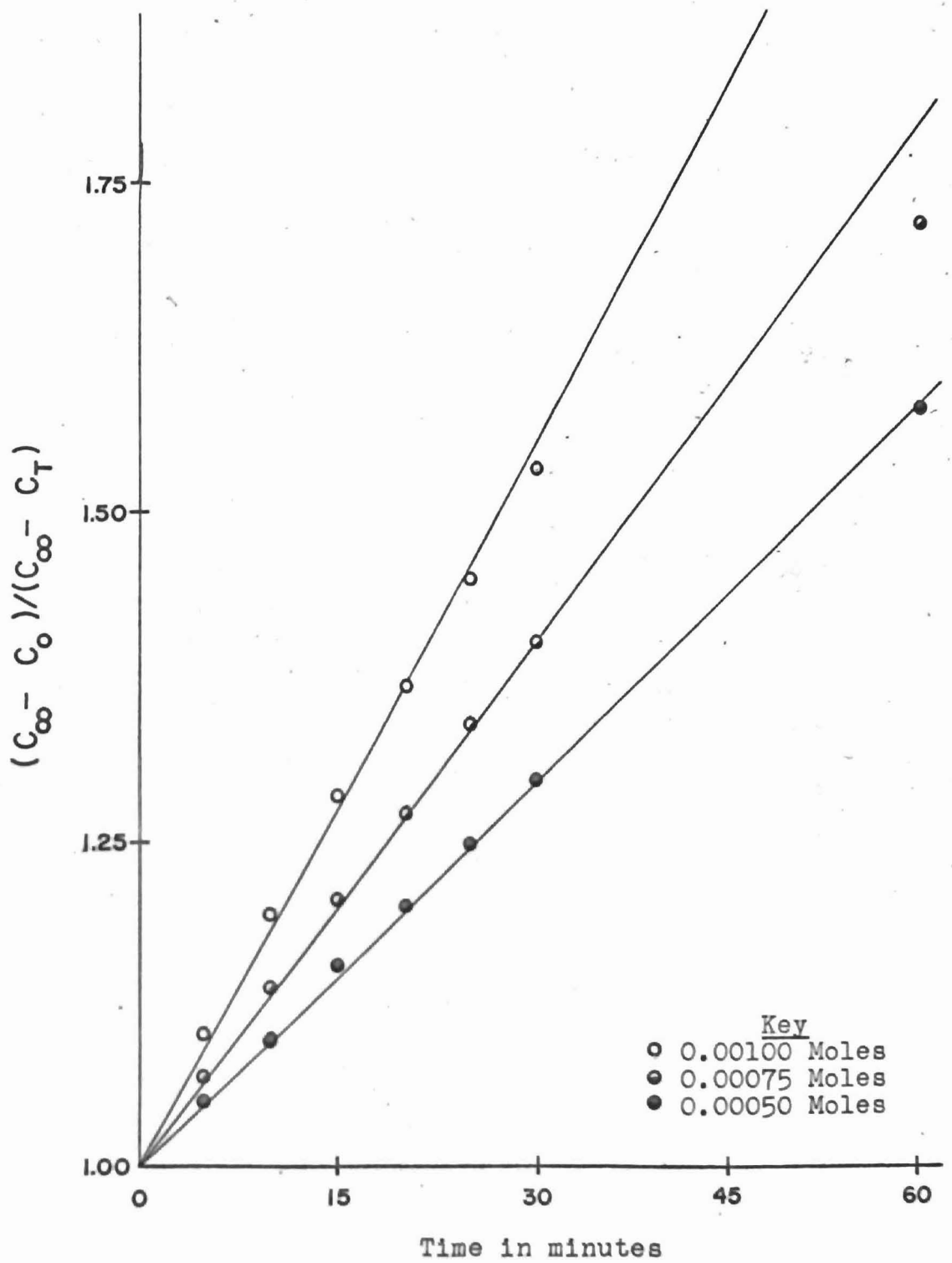

Figure 4. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 1 at 25.0° Centigrade.

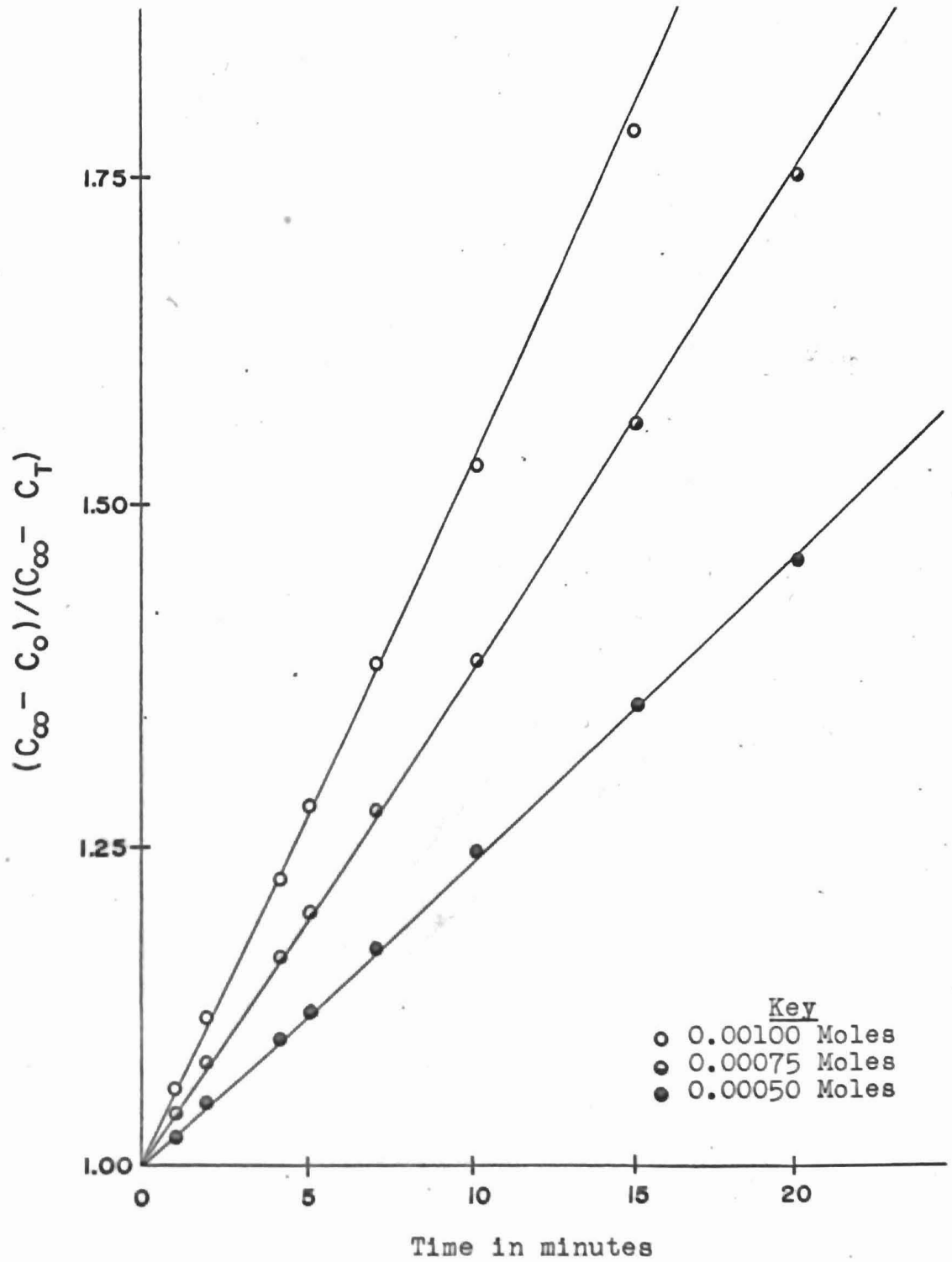

Figure 5. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 1 at 40.0° Centigrade.

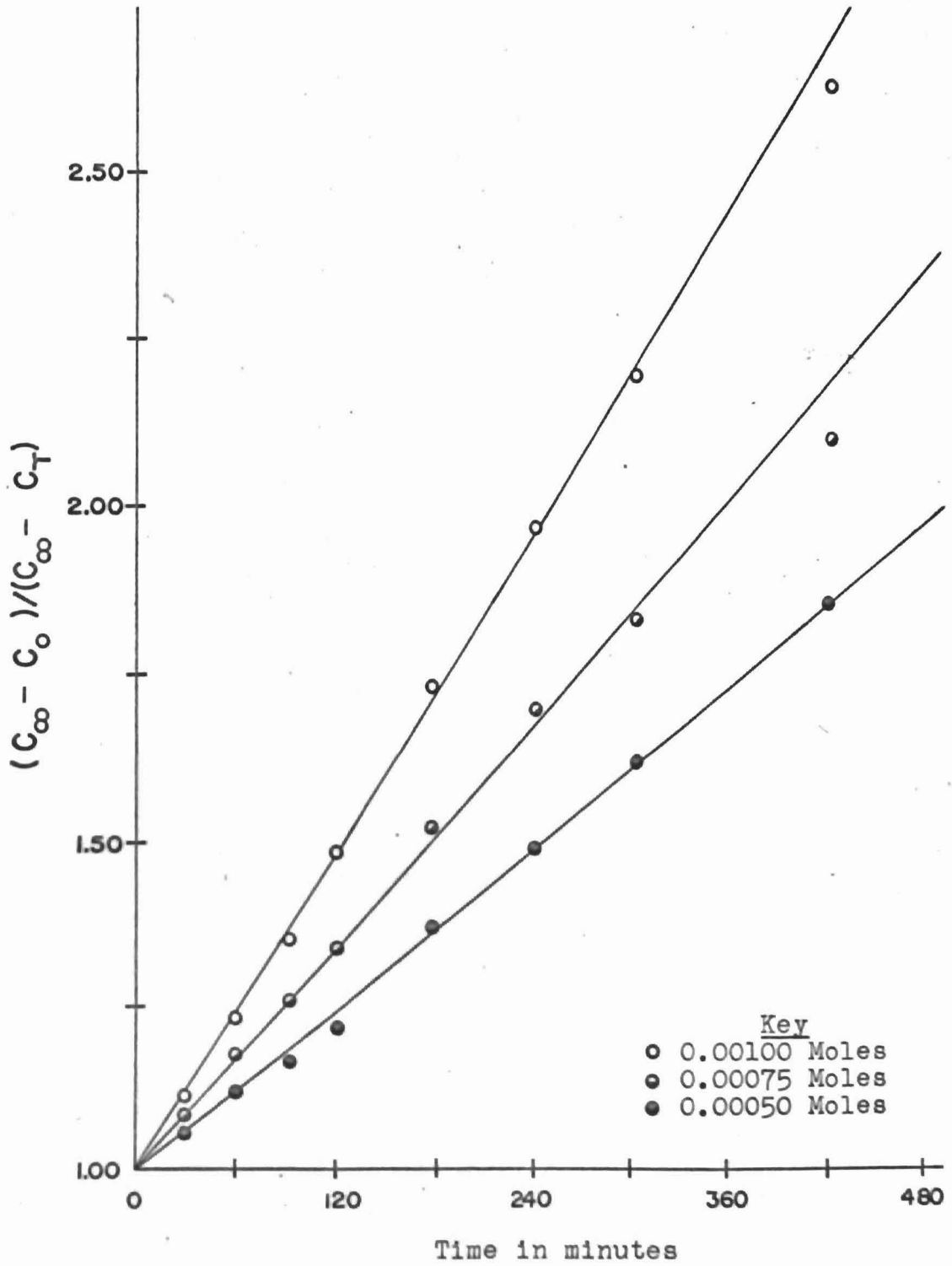

Figure 6. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 2 at 0.1° Centigrade.

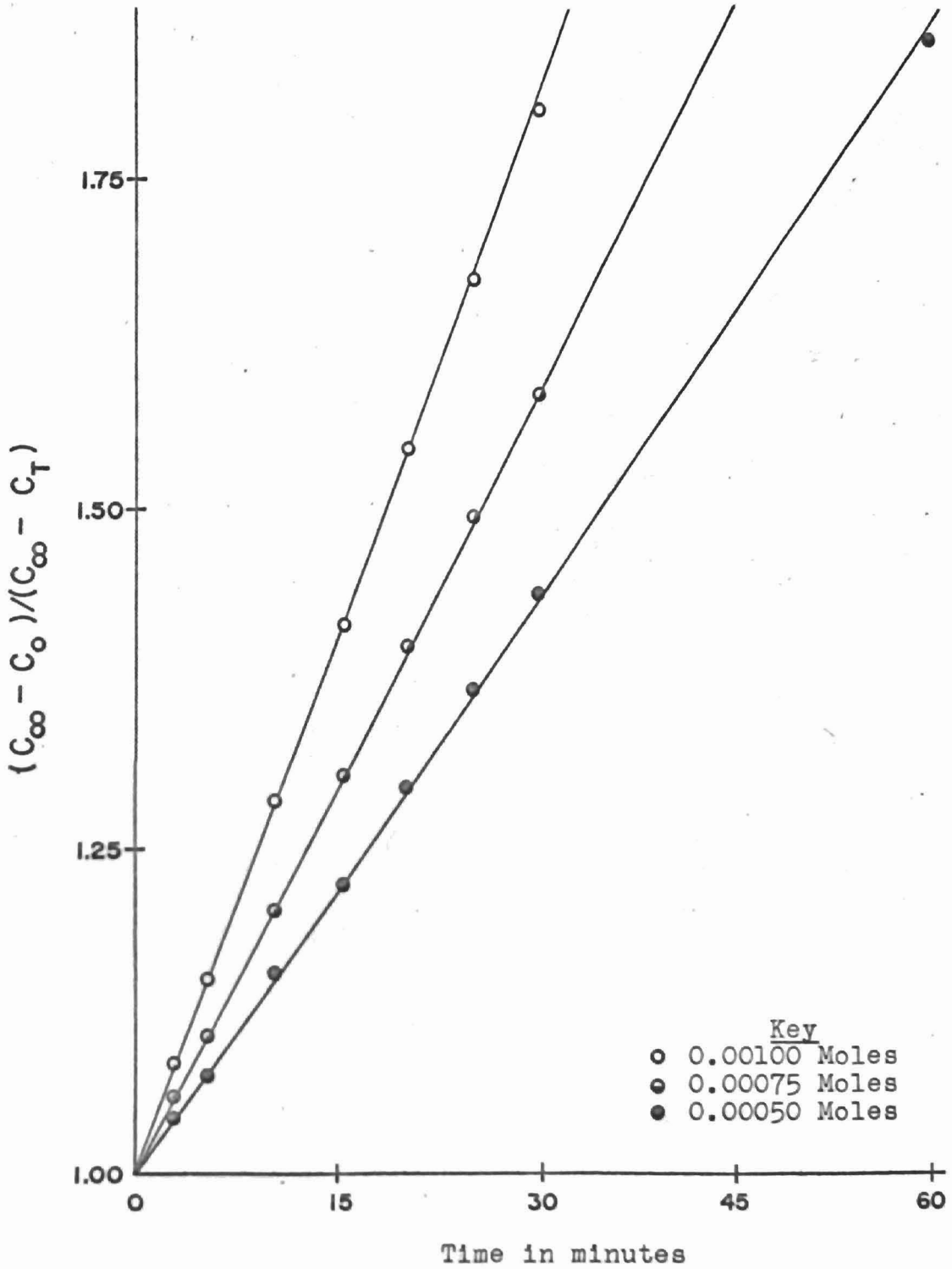

Figure 7. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 2 at 25.0° Centigrade.

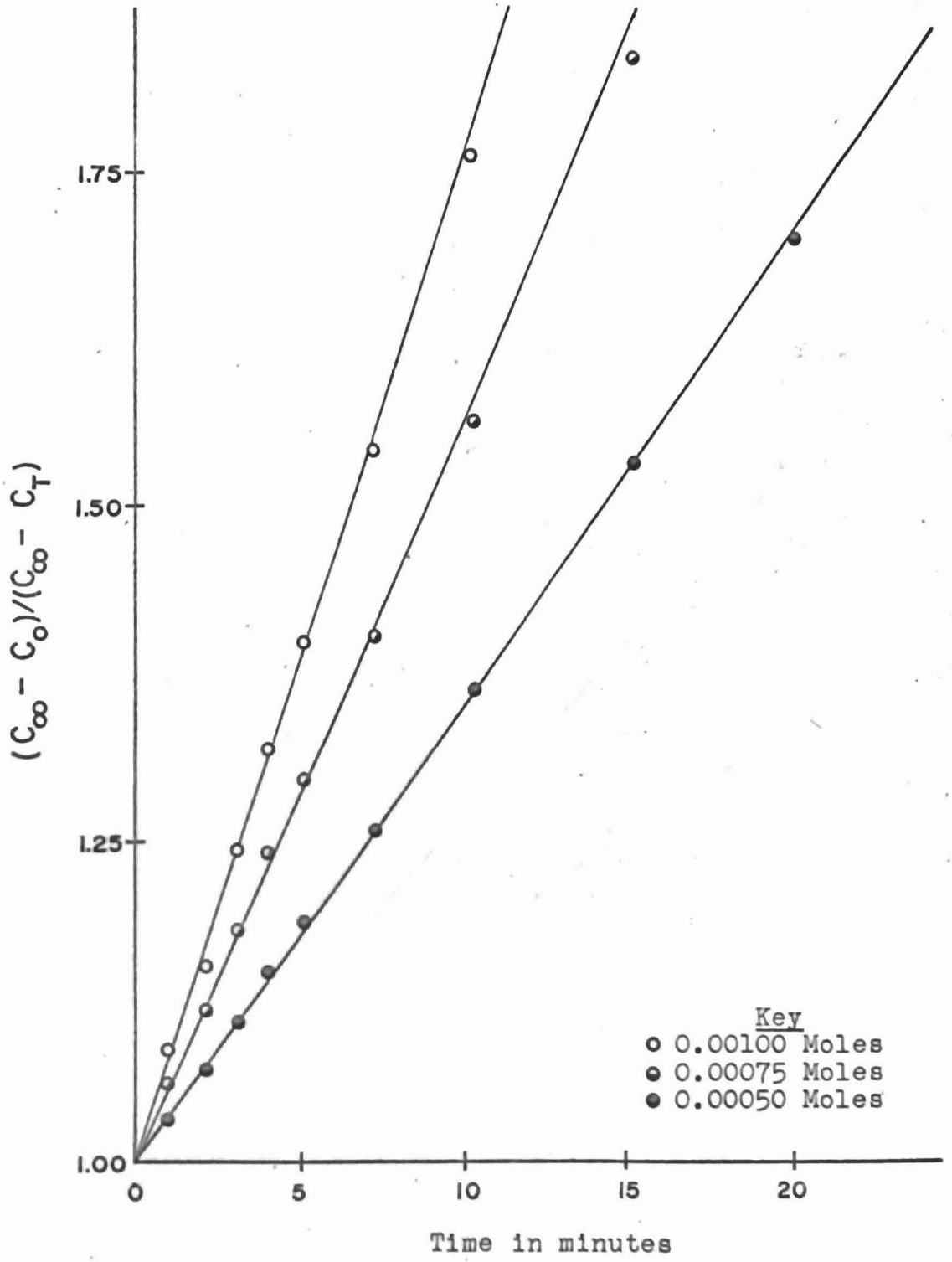

Figure 8. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 2 at 40.0° Centigrade.

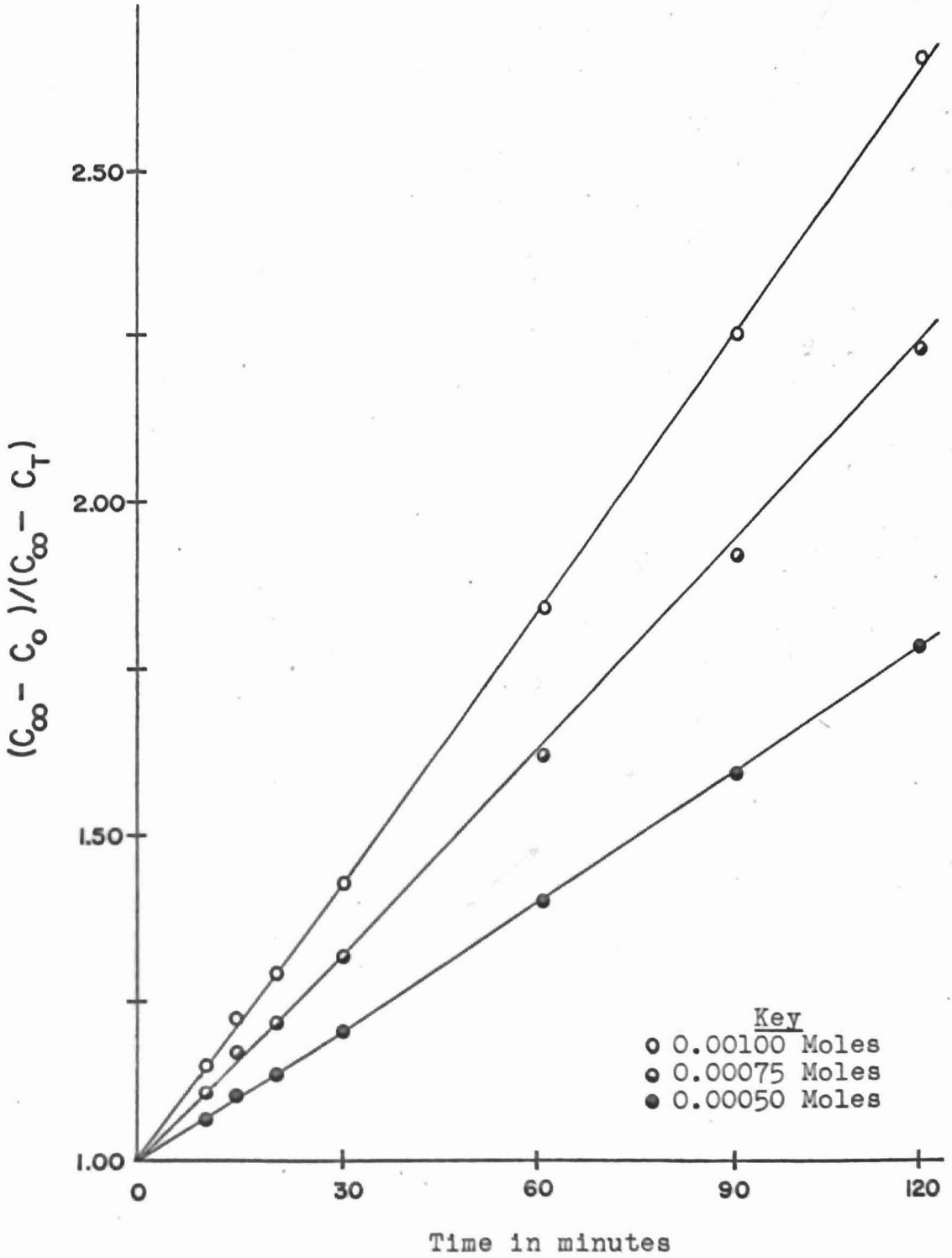

Figure 9. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 1 at 0.1° Centigrade.

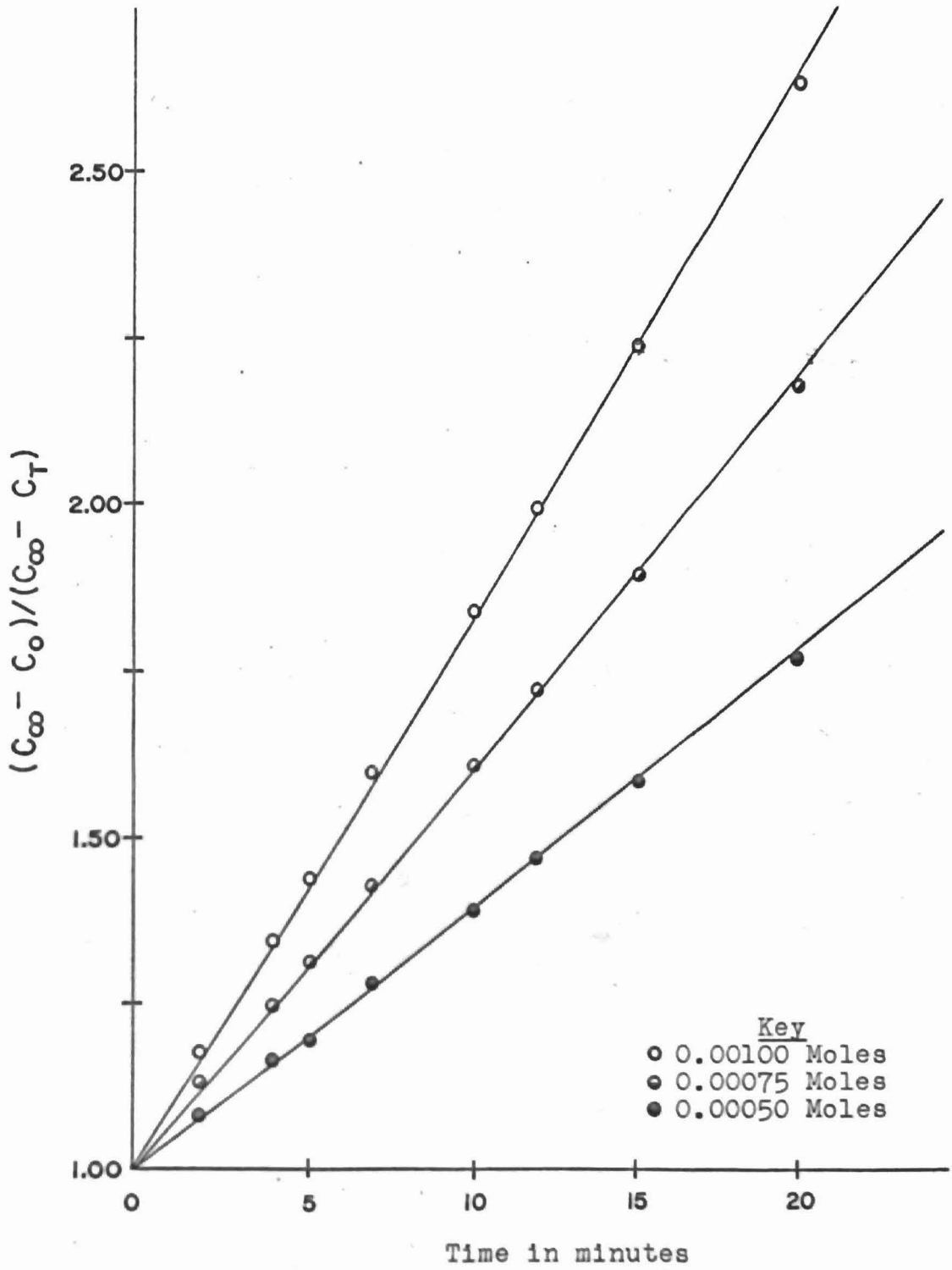

Figure 10. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 1 at 25.0° Centigrade.

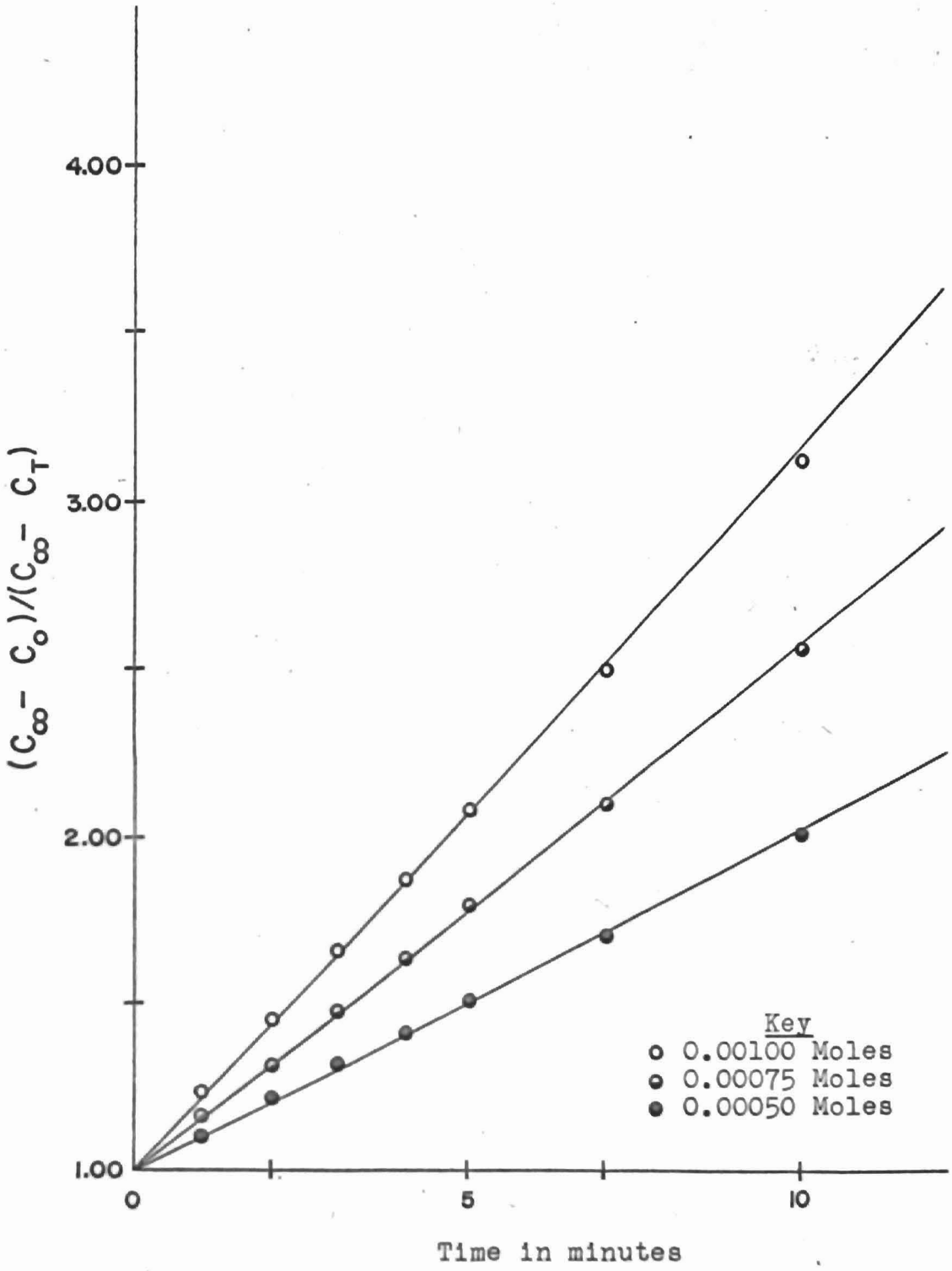

Figure 11. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 1 at 40.0° Centigrade.

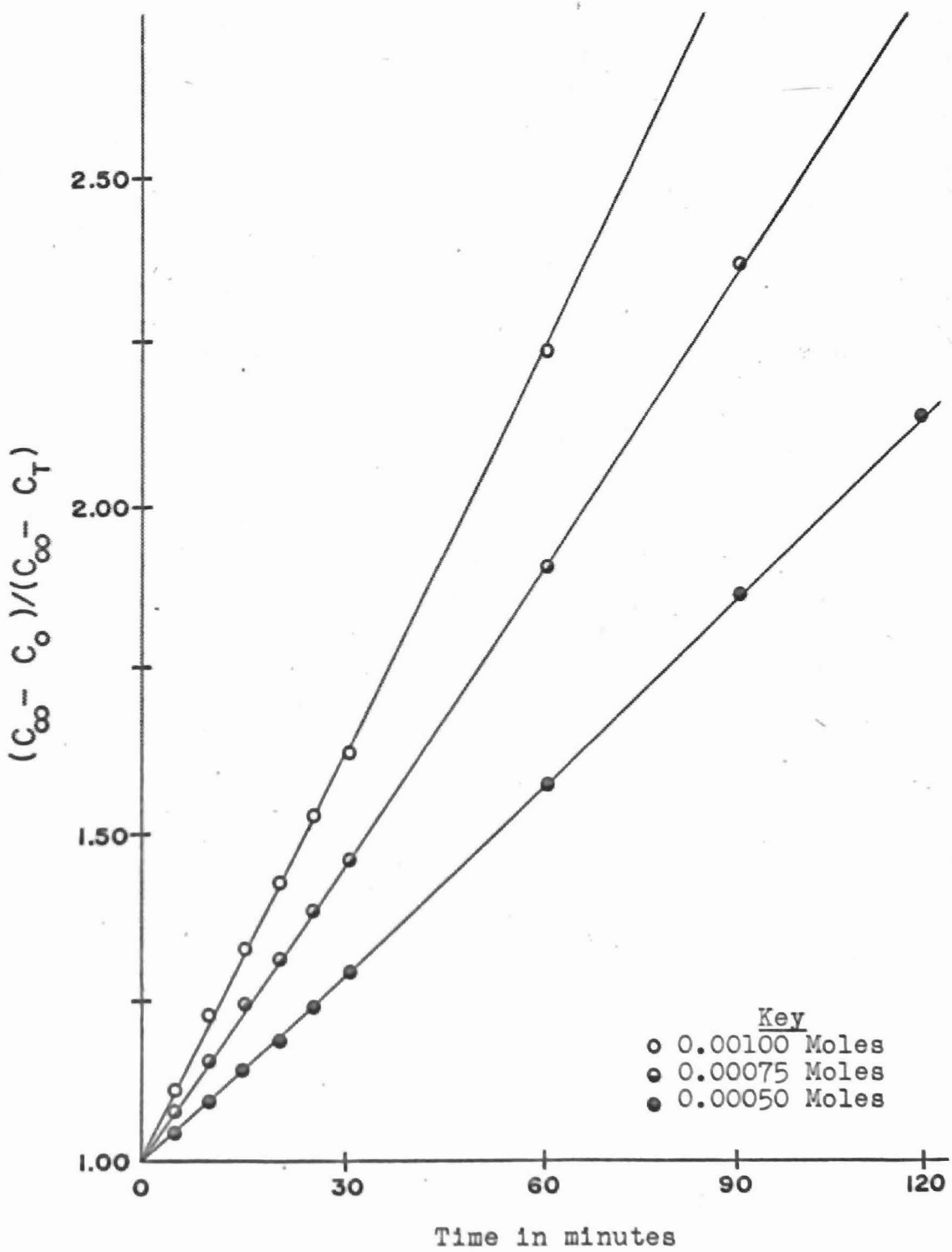

Figure 12. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 2 at 0.1° Centigrade.

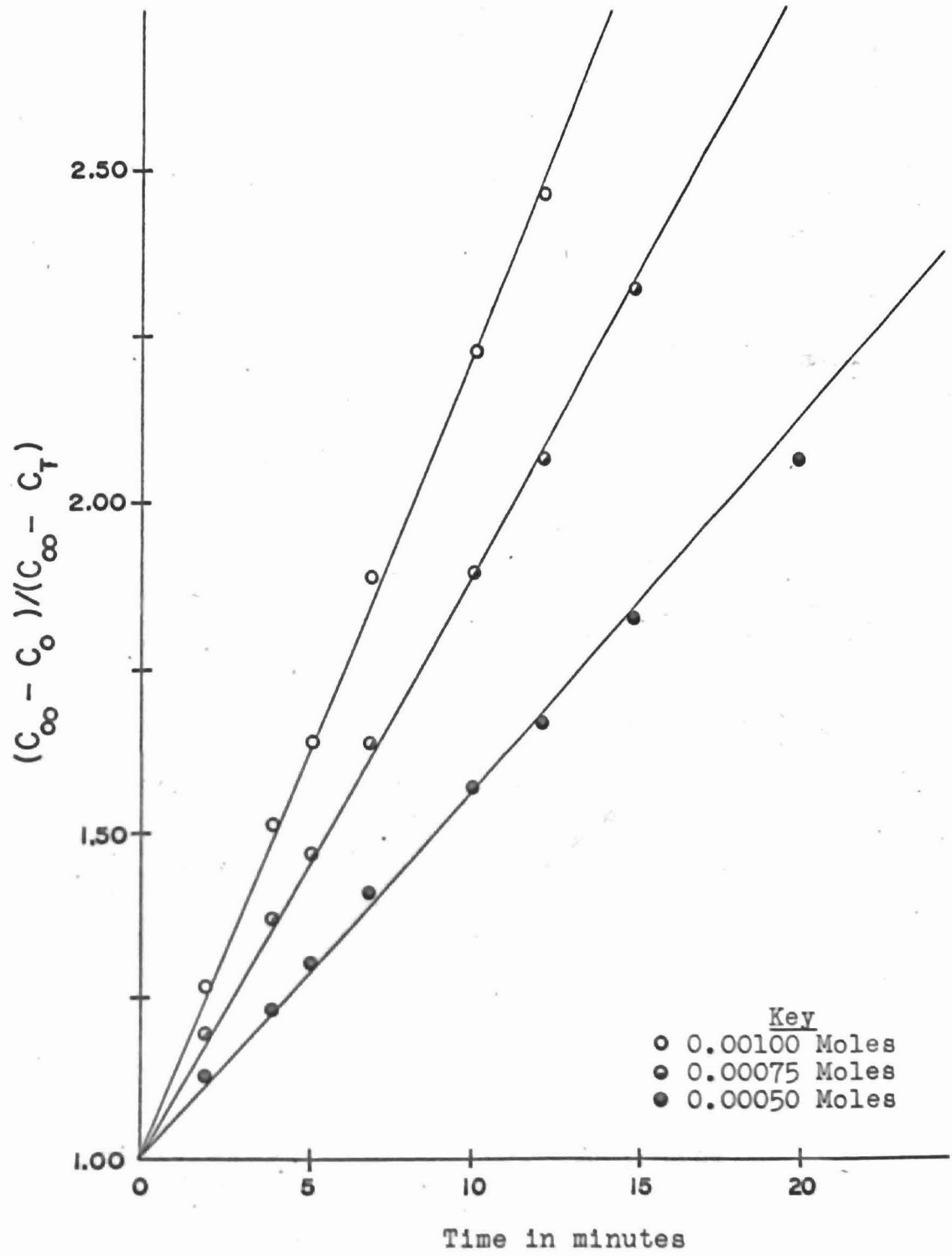

Figure 13. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 2 at 25.0° Centigrade.

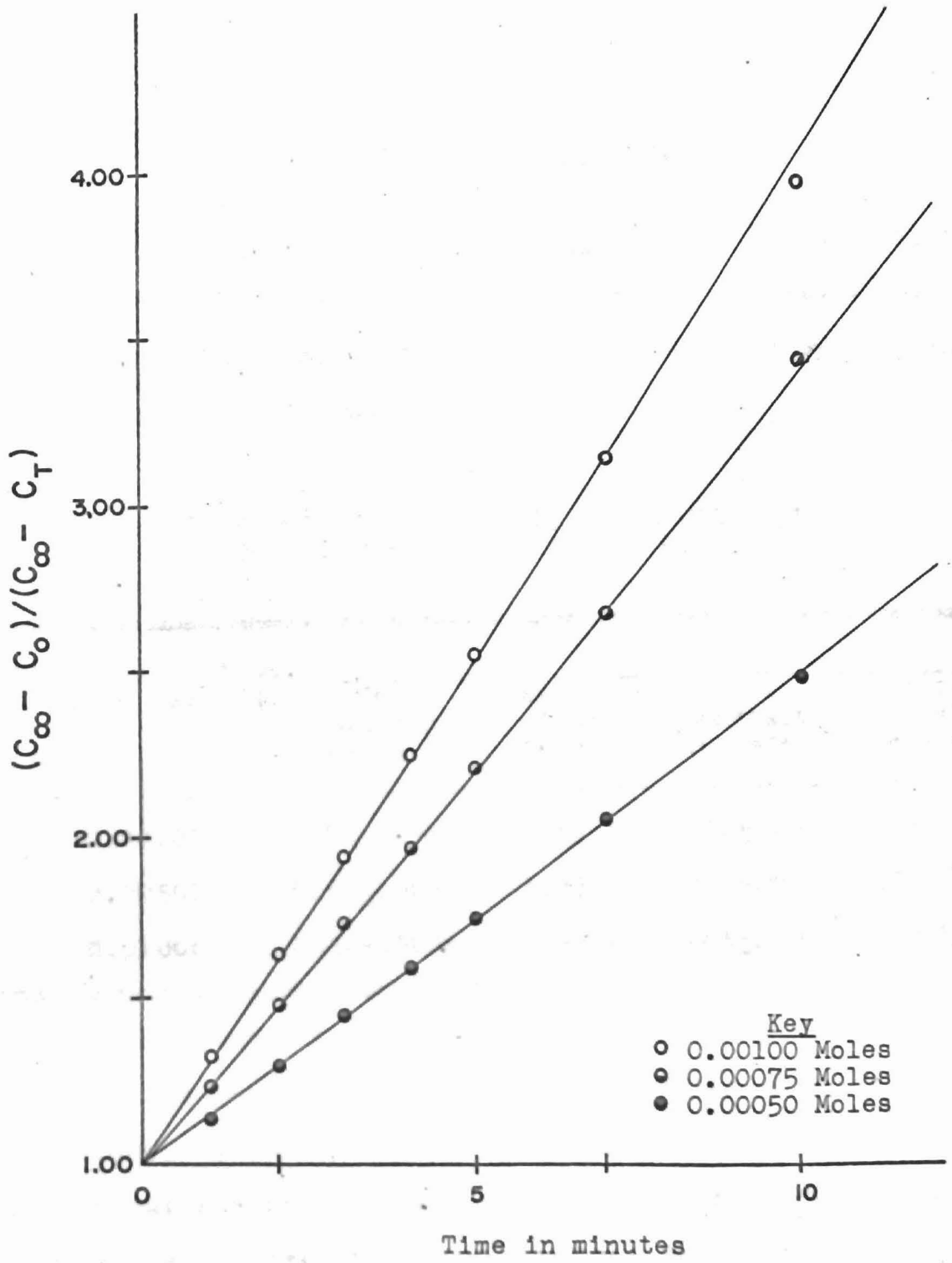

Figure 14. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 2 at 40.0° Centigrade.

CHAPTER IV

CONCLUSIONS AND DISCUSSIONS

Determination of Cell Constants. The reproducibility of cells 1 and 2 are listed in Table XLIV. The deviation which was found limited the accuracy of the measurements to four significant figures.

TABLE XLIV

REPRODUCIBILITY OF CELL 1 AND CELL 2 AT VARIOUS CONCENTRATIONS OF KCl AT 25.0° C

KCl concentration in moles per liter	Cell 1		Cell 2	
	Cell Constant in cm^{-1}	Resistance of cell in ohms	Cell Constant in cm^{-1}	Resistance of cell in ohms
0.00100	1.3886±.0009	9455	.1221±.0002	835.0
0.00500	1.4154±.0030	1973	.1246±.0001	173.7
0.01000	1.4032±.0002	993.1	.1245±.0002	88.1

The change in cell constants with change in concentration was thought to be due to preparation of the standard solutions. Three different solutions were prepared and the same results were obtained. The deviations for both cells were quite consistant meaning that the cell constant was reliable and reproducible both before and after the measurement of the reaction rates. No attempt was made to check

reproducibility between measurements of the iodo and bromo reactions, thus, the change in the cell constant is an overall effect. Since the deviation is so small, the error between runs could not be any greater. The measurements made after the completion of the reactions were consistantly higher for cell 1 and consistantly lower for cell 2. Since the errors were small, they probably are caused by experimental determinations. At any rate, since the cells were reproducible, work was started on the determination of reaction rates. This involved, as stated before, a measurement of the change in cell conductance with time, determination of the conductivity ratio, finding the slope of the linear relationship between the conductivity ratio and time and the values for the rate constants.

The 1-chloro-2,4-dinitrobenzene reaction. This reaction was carried out to check the equipment and to relate this study to that of Charles O. Frank. The data obtained for the reaction at 25.0° C can be found in Tables II through VII and in Figures 1 and 2. The conductivity ratios and recorded times were plotted and the slopes of the lines, y-intercepts, rate constants, and half-lives were recorded in Table XLV.

TABLE XLV

SLOPES, Y-INTERCEPTS, RATE CONSTANTS, AND HALF-LIVES OF THE CHLORO REACTION AT 25.0° C

Moles of 2,4 dinitrochloro-benzene in 40.0 ml. call volume	slope	y-intercept	k (liter mole^{-1} minute^{-1})	$t_{\frac{1}{2}}$ (minutes)
		Cell 1		
.00100	.0781	1.019	1.562	12.80
.00200	.1712	1.009	1.712	5.84
.00250	.2200	0.997	1.760	4.55
Concentration in moles/28 ml. cell volume				
		Cell 2		
.00100	.1114	1.051	1.560	8.98
.00200	.2515	1.042	1.761	3.96
.00250	.3150	1.113	1.764	3.17

Frank[1] obtained the rate constant of 1.744±.080 liter mole^{-1} minute^{-1} as compared with 1.686±.084 liter mole^{-1} minute^{-1} for this study. The values were consistantly lower in this work but still were within the range of Frank's work. The results of this comparison shows that the measurement of reaction rate by a hange in conductance, as opposed to a change in resistance, is at least comparable. Since all resistance measurements must be changed into conductance for

[1]Frank, op. cit., p. 62.

use in the conductance ratio, it is obvious that the conductance measurement is more convenient. It was found that in a conductivity measurement that the variance increased with an increase in conductance. This is a reverse from what was found in the resistance study where the variance decreased with decreasing resistance. However, if one looks at the error in parts per thousand, similar results are obtained in both measurements, namely, the precision of the measurement becomes greater as the reaction slows down whether resistance or conductance is used to obtain the values.

Unfortunately, the individual conductance ratios obtained from the data are not comparable because slightly different concentrations were used in the two studies. However, a comparison can be made, as is done in Table XLVI, between the infinity conductances at different concentrations. A similar comparison should exist between the concentrations of the piperidine solutions but discrepencies in Frank's data did not permit the comparison.

The comparison of the infinity conductances shows the consistancy of both measurements by the close agreement of the values. The greater consistancy in the infinity values obtained by this study seem to indicate that these values are taken closer to the equilibrium point.

TABLE XLVI

RATIOS OF THE INFINITY CONDUCTANCES FOR DIFFERENT CONCENTRATIONS OF 1-CHLORO-2,4-DINITROBENZENE AT 25.0° C

Concentration ratio in moles per cell volume	This Study		Work cited[1]	
	Cell 1	Cell 2	Cell B	Cell A
	C_∞/C_∞			
.0025/.0020	1.19	1.17	1.13	1.20
.0020/.0010	1.70	1.70	1.73	1.64
.0025/.0010	2.02	2.03	1.97	1.98

Since the RC-18 conductivity bridge has a limit of 11,111 micromhos, care must be taken to insure the conductances remain within the limit. The chloro reaction reached 10,200 micromhos at 0.0025 moles per volume of cell 2 at 25°.

The 1-iodo-2,4-dinitrobenzene reaction. Since the values were in agreement, it seemed possible that the other halo-substituted dinitrobenzenes might give reaction constants in the same way. The data obtained on the reaction between 1-iodo-2,4-dinitrobenzene and piperidine is recorded in Tables VIII through XXV and Figures 3 through 8. The conductance range for all concentrations and temperatures was approximately 600 micromhos for cell 1 and 9,100

[1] Ibid., pp. 32-35; 41-43.

micromhos for cell 2. Due to the more dilute solutions, the conductances were not as high as those obtained from the chloro reaction. The errors in the individual measurements showed that, generally, the errors increased with increasing temperature and concentration. This again is misleading as the error in parts per thousand was less for the higher temperatures and concentrations. It may be noted that the errors at 0.1° C were much lower than other data showing that the special procedure followed at the lower temperature has some merit as an aid for very slow reactions or very dilute concentrations.

The increase in conductance with temperature was expected because of the increased energy of the system. The increased concentration of product showed an increase in conductance with time due to the growing amounts of piperidinium halide in the solution.

To show that the conductance ratio $C_\infty - C_o / C_\infty - C_t$ would not be affected by temperature, the ratio of the conductances at zero time and infinite time for the high and low temperatures were made and the values appear in Table XLVII. Again these values could be used to approximate the equilibrium point of the reaction at any temperature.

TABLE XLVII

RATIO OF THE CONDUCTANCES FOR THE IODO REACTION AT 40.0° C to 0.1° C

Concentration of piperidine in moles/liter	Cell 1		Cell 2	
	C_o/C_o	C /C	C_o/C_o	C /C
0.100	2.22	2.12	2.19	2.12
0.150	2.24	2.28	2.27	2.18
0.200	2.23	2.24	2.22	2.20

Frank found similar results with his work on the chloro homolog. The relationship between the conductances indicates that the temperature effect on the conductance was linear and did not affect the conductivity ratio C $-C_o$/C $-C_t$ as all values increased with temperature. An attempt was made to determine the relationship of C_t with temperature but the results were not linear due to the change in reaction rate at the elevated temperatures.

In the equation:

$$\frac{C - C_o}{C - C_t} = 2kat + 1$$

one can see that as C_t increases, C $- C_t$ decreases making the conductance ratio increase with time. A plot of the conductance ratio versus time shows a linear relationship which has a slope of 2ka and a y-intercept of 1. Table XLVIII lists the slopes and y-intercepts for the three

temperatures employed for the 1-iodo-2,4-dinitrobenzene reaction with piperidine.

TABLE XLVIII

SLOPES AND Y-INTERCEPTS OF CONDUCTANCE CURVES FOR THE 1-IODO-2,4-DINITROBENZENE REACTION AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Moles of iodo for 40.0 ml. cell volume	Slope			y-intercept		
	0.1°C	25°C	40°C	0.1°C	25°C	40°C
			Cell 1			
0.00050	.00146	.0095	.0240	0.998	1.004	1.000
0.00075	.00210	.0115a	.0370	0.999	1.014a	1.010
0.00100	.00277	.0172	.0517	0.998	1.016	1.020
Concentration in moles/28 ml. cell volume			Cell 1			
0.00050	.00201	.0140	.0345	0.998	1.009	1.006
0.00075	.00290	.0189	.0570	0.998	1.012	0.996
0.00100	.00393a	.0262	.0764	1.004a	1.016	1.004

a - These values have been revised by rejection of one conductance figure.

The y-intercept values, have errors up to twenty parts per thousand which indicates a maximum of three place accuracy in the slope of the line. The rejection of the two points described above was based on the deviation of the y-intercept from its actual value of 1.000. These points,

being toward the end of the reaction, influenced the y-intercept because their values were sometimes twice as large as earlier points. For example, a point was rejected at sixty minutes where the previous point was taken at thirty minutes. To avoid this rejection, more points should have been made between thirty and sixty minutes to lessen the effect of the last point with its large influence on the slope.

From the slopes of the conductance curves, the specific rate constants and half-lives may be calculated. The specific rate constant (k) may be found by dividing the slope by 2a where a is the concentration in mole liter^{-1}. The half-life is the reciprocal of the slope. The rate constants and half-lives for the 1-iodo-2,4-dinitrobenzene and piperidine reaction are calculated and listed in Table XLIX.

The average rate constants for both cells at 0.1°C, 25.0°C, and 40.0°C are 0.0558, 0.3598, and 1.007 liter mole^{-1} minute^{-1}, respectively. There is no literature with which these results might be compared. It would be interesting to see if the same results would be obtained through a chemical or spectrophotometric analysis.

The half-lives recorded are equal to the conductance ratio when the ratio has the value of 2.00. Very close agreement with these values indicates the reliability of the measurements.

TABLE XLIX

SPECIFIC RATE CONSTANTS AND HALF-LIVES OF THE 1-IODO-2, 4-DINITROBENZENE REACTION AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Moles of iodo for 40.0 ml. cell volume	k (liter mole^{-1} minute^{-1})			$t_{\frac{1}{2}}$ (minutes)		
	0.1°C	25°C	40°C	0.1°C	25°C	40°C
			Cell 1			
0.00050	.0583	.3800	0.960	685.87	105.27	41.67
0.00075	.0560	.3248	0.987	476.41	82.10	27.03
0.00100	.0554	.3430	1.032	360.75	58.34	19.33
Concentration in moles/28 ml. cell volume						
			Cell 2			
0.00050	.0563	.3931	0.967	497.51	71.22	28.96
0.00075	.0541	.3521	1.064	344.94	53.05	17.55
0.00100	.0550	.3661	1.034	254.45	38.24	13.53

The 1-bromo-2,4-dinitrobenzene reaction. The data obtained from the reaction between 1-bromo-2,4-dinitrobenzene and piperidine is recorded in Tables XXVI through XLIII and Figures 9 through 14. The conductance range over all concentrations and temperatures was slightly less than the iodo reaction. Cell 1 had a maximum conductance of 538 micromhos while cell 2 had a maximum of 8000 micromhos.

Error in the recorded conductances was more random than for the iodo indicating better precision measurement. The percentage of error and the variance were all less for a specific concentration at a specific temperature for the bromo reaction. Since the bromo was the last reaction to be performed during the study, an increase in familiarity with the equipment may have accounted for the better values. The highest error recorded for the bromo reaction was for 0.00075 moles at 25° C in both cells. The least error was found in the measurements of the 0.00050 moles at 0.1° C.

The conductance ratios increased, as expected, with increasing temperature and/or concentration. Table L relates the temperature effects on the conductance at zero time and infinite time.

TABLE L

RATIO OF THE CONDUCTANCES FOR THE BROMO REACTION AT 40.0° C to 0.1° C.

Concentration of piperidine in moles/liter	Cell 1		Cell 2	
	C_o/C_o	C_∞/C_∞	C_o/C_o	C_∞/C_∞
0.100	2.22	2.22	2.19	2.16
0.150	2.24	2.19	2.27	2.09
0.200	2.23	2.17	2.22	2.16

Again, the values are quite consistant, indicating that the conductance ratio is reliable with a change in temperature. The change in conductance ratio is partially

due to an increase in all quantities. The ratio of infinite conductances for 0.150 molar piperidine in cell 2 is very low which may be due to an error in measurement of the conductance of the 40° C infinity reading. A check shows that the corresponding value for a 40°/25° ratio is also low. Thus, these values are useful in determining whether or not the proper conductances are obtained for infinite time and zero time.

The change in conductivity ratio with a change in time gives a slope of 2ka and a y-intercept of 1 as indicated previously. The values obtained for the bromo reaction are listed in Table LI.

The y-intercept values are closer to the value of 1.00 than the iodo reaction although many of the slopes had to be revised as the conductance ratio became too high with increasing time. Cell 2 has most of the values that were corrected which leads one to believe that the conductance is too high for the later times during the reaction. With the corrections, the y-intercept values become closer to the accepted 1.00 and the slopes became more uniform.

TABLE LI

SLOPES AND Y-INTERCEPTS OF CONDUCTANCE CURVES FOR THE 1-BROMO-2,4-DINITROBENZENE REACTION AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Moles of bromo for 40.0 ml. cell volume	Slope			y-intercept		
	0.1°C	25°C	40°C	0.1°C	25°C	40°C
			Cell 1			
0.00050	.00654	.03744	.09864	1.001	1.009	1.011
0.00075	.01023	.05870	.1573	1.004	1.008	1.006
0.00100	.01381	.08114a	.2140	1.008	1.012a	1.012
Concentration in moles/28 ml. cell volume			Cell 2			
0.00050	.00948	.04849a	.1485	1.005	1.051a	1.006
0.00075	.01506	.08789a	.2472a	1.008	1.011a	0.989a
0.00100	.01381	.1264a	.2928a	1.008	0.972a	1.051a

a - These values have been revised by rejection of one or more conductance figure.

From the slopes listed in Table LI, the corresponding rate constants and half-lives are calculated and recorded in Table LII.

TABLE LII

SPECIFIC RATE CONSTANTS AND HALF-LIVES OF THE 1-BROMO-2, 4-DINITROBENZENE REACTION AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Moles of bromo for 40.0 ml. cell volume	k (liter mole^{-1} minute^{-1})			$t_{\frac{1}{2}}$ minutes)		
	0.1°C	25°C	40°C	0.1°C	25°C	40°C
			Cell 1			
0.00050	.2616	1.498	3.946	152.92	26.71	10.14
0.00075	.2729	1.566	4.196	97.72	17.04	6.35
0.00100	.2762	1.623	4.280	72.40	12.32	4.67
Concentration in moles/28 ml. cell volume			Cell 2			
0.00050	.2654	1.358	4.161	105.48	20.62	6.73
0.00075	.2811	1.715	4.611	66.40	10.88	4.04
0.00100	.2916	1.769	4.099	47.98	7.88	3.42

The average rate constants were 0.2748, 1.588, and 4.216 liters mole^{-1} minute^{-1} for 0.1° C, 25.0° C, and 40.0° C, respectively. No literature reports this reaction in ethanol leaving no comparison between the physical and the chemical methods. The half-life values correspond closely to the conductance ratio of 2.00 giving reliability to the measurements.

Energy of activation and enthalpy relationships. The activation energy is the energy required to form the activated complex which must be attained if a reaction is to occur. The attainment of this activated state is capable, as is the rate of reaction, of determining the halogen reaction series which will be discussed later. The energy of activation obtained from the integrated Arrhenius equation was found to be 12.28 Kcal. for the iodo reaction. A value of 11.58 Kcal. was obtained for the bromo reaction. A plot of the logarithm of the rate constants against the reciprocal of the absolute temperature is a linear relationship which is shown in Figure 15 for the iodo reaction and Figure 16 for the bromo reaction.

The entropy value for the reactions was determined by the equation:

$$\log k = \frac{S^*}{2.303\ R} - \frac{E}{2.303\ RT} + \log \frac{RT}{Nh} .$$

An increase in entropy is signified by a negative quantity indicating an increase in the disorder of a system. The larger the negative value, the quicker the reaction proceeds which also gives an indication of the halogen order of reaction. The change in entropy for the iodo system was -19.25 calories degree^{-1} mole^{-1}. The change in entropy for the bromo system was -18.74 calories degree^{-1} mole^{-1}.

The reaction series for 1-halo-2,4-dinitrobenzene with

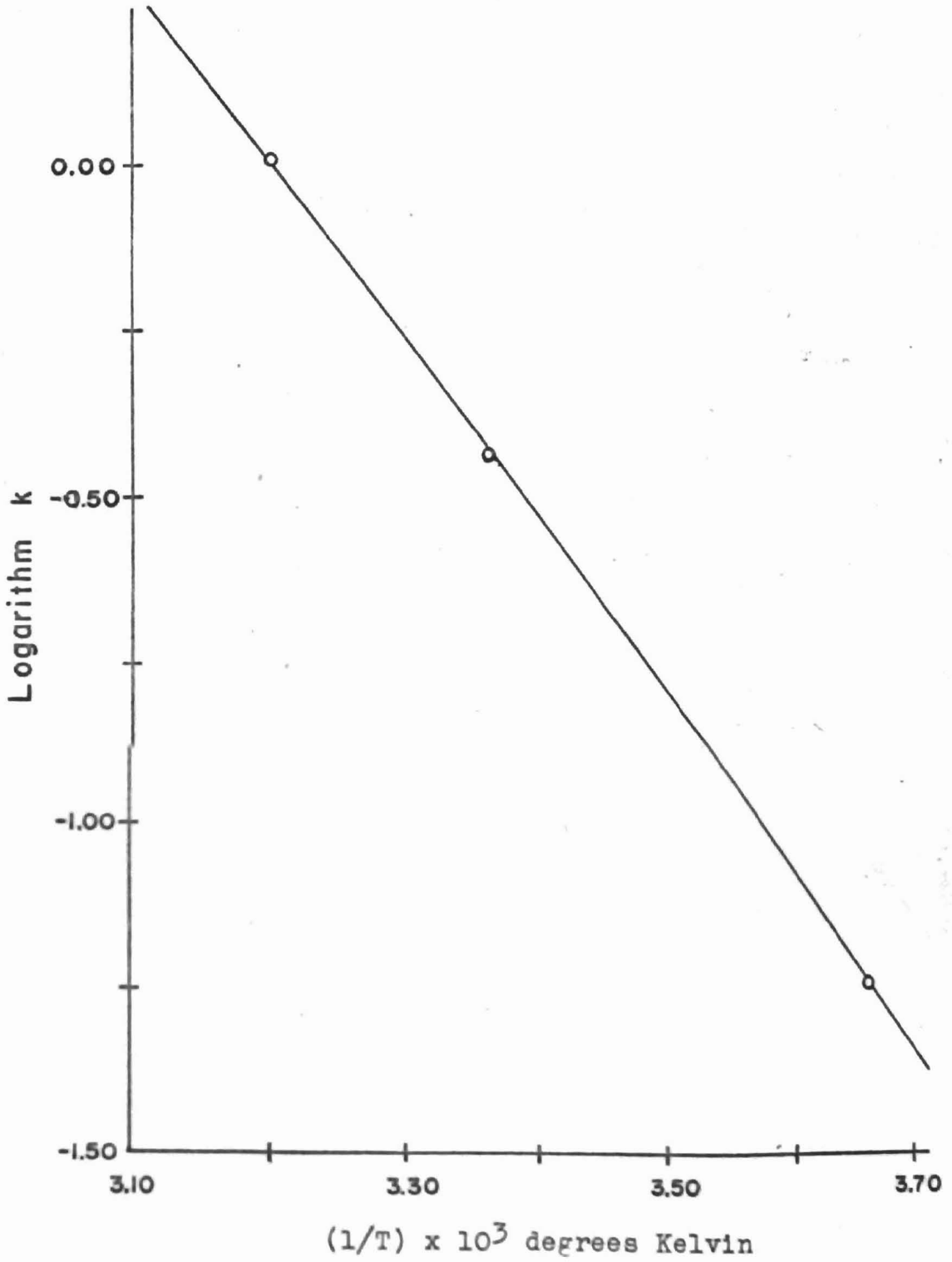

Figure 15. Variation of logarithm k with the reciprocal of the absolute temperature for the 1-iodo-2,4-dinitrobenzene reaction.

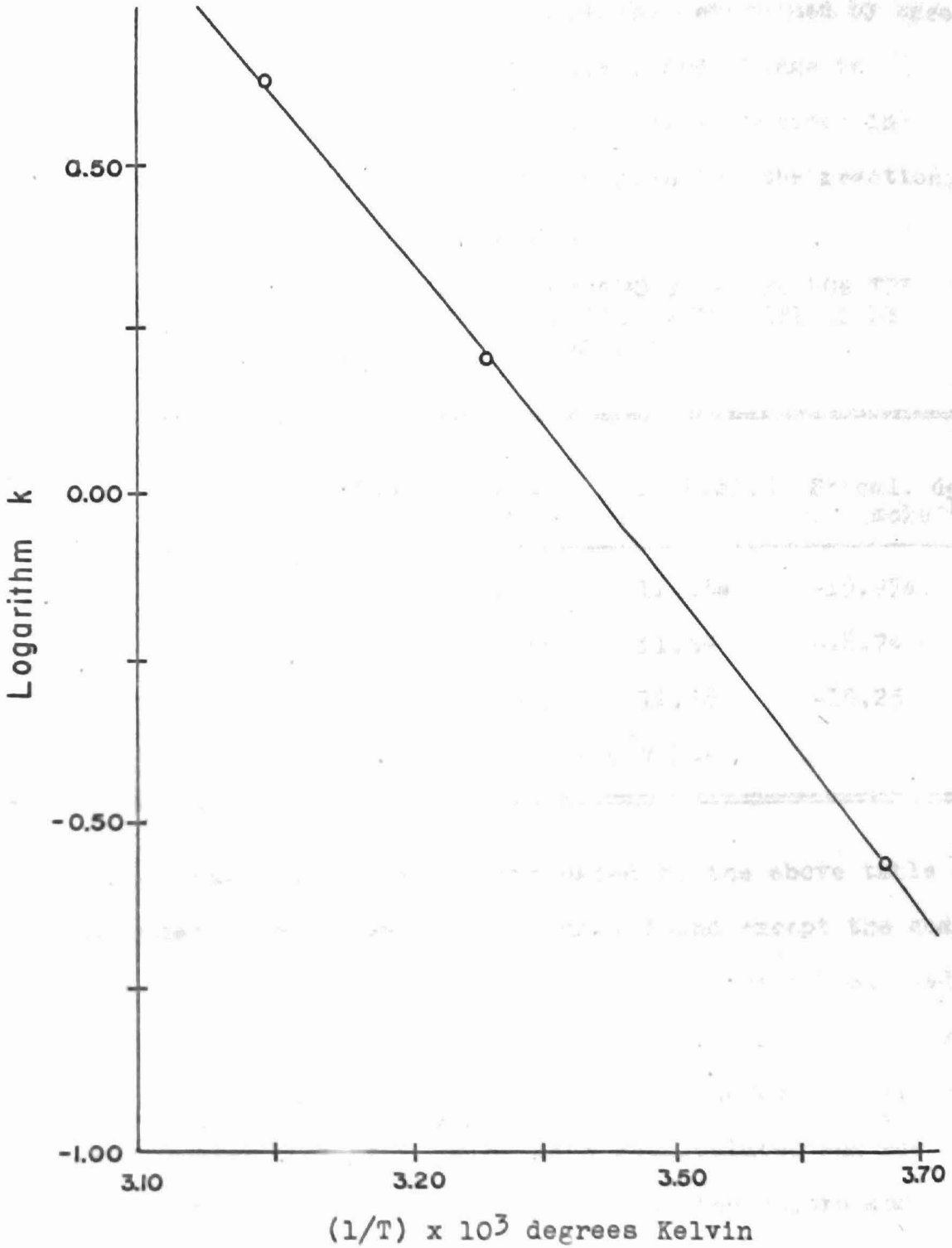

Figure 16. Variation of logarithm k with the reciprocal of the absolute temperature for the 1-bromo-2,4-dinitrobenzene reaction.

piperidine in 95 per cent ethanol can be determined by specific rate constants, change in enthalpy, and change in entropy. Comparisons of these values are summarized in Table LIII in order to establish a series for the reaction.

TABLE LIII

RATE CONSTANTS, ENTHALPY, AND ENTROPY VALUES FOR THE 1-HALO-2,4-DINITROBENZENE REACTION WITH PIPERIDINE IN 95 PER CENT ETHANOL

Halogen group	k (liter mole^{-1} degree^{-1}) 0.1°C	25°C	40°C	E (Kcal.)	S*(cal. deg.$^{-1}$ mole^{-1})
Chloro-[1]	.3188	1.744	4.423	11.16a	-19.97a
Bromo-	.2748	1.588	4.216	11.59	-18.74
Iodo-	.0056	0.360	1.007	12.28	-19.25

aCorrected from Frank's values

The reaction series as indicated by the above table is in the order Cl > Br >> I in all data found except the change in entropy. This is very surprising since the values used to calculate the entropy are in the correct order. Frank lists values of 10.66 kcal. for the activation energy and -21.84 calories degree^{-1} mole^{-1} which were recalculated and now show an even closer relationship between the chloro and bromo. Chapman and Parker report that the 1-fluoro-2,

[1] Ibid., pp. 62-65.

4-dinitrobenzene reaction with piperidine in 99.8 per cent ethanol is 50 to 100 times faster than the chloro reaction.[1] The series would be completed in the order: F >> Cl > Br >> I.

The conductometric analysis of 1-bromo-and 1-iodo-2,4-dinitrobenzene with piperidine was carried out at three temperatures to complete the reactivity series. Other work that has been done by a chemical analysis has been cited which may be tried by a conductometric analysis.

A continuous recording device would make reactions simpler for then an infinite number of points could be taken and the reaction could be recorded without the problem of zeroing the Wheatstone Bridge.

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[1] N. B. Chapman, R. E. Parker, and P. W. Soanes, "Reactivity of Halonitrobenzenes and of 1-Fluoro-2,4-dinitrobenzene," Chemistry and Industry (1951), 148.

CHAPTER V

SUMMARY

The purpose of this thesis was to determine the rate of reaction of 1-bromo- and 1-iodo-2,4-dinitrobenzene and piperidine in 95 per cent ethanol at various temperatures and concentrations by a conductometric process. The 1-chloro-2,4-dinitrobenzene reaction with piperidine was rechecked at 25.0° Centigrade to relate the results of this study to a previous work. Also, the establishment of a halogen reactivity series for the reaction was intended.

The reaction between 1-chloro-2,4-dinitrobenzene and piperidine in 95 per cent ethanol was followed conductometrically at 25.0° C. on an RC-18 conductivity bridge. The conductance at time t was used to find the conductivity ratio which varied directly with time, verifying the equation for the determination of the reaction constants. The specific rate constant was found to be 1.686 liter $mole^{-1}$ $minute^{-1}$ which compared closely with the value of 1.744 liter $mole^{-1}$ $minute^{-1}$ found by Frank.[1] The error for the individual conductance measurements was found to increase with time rather than decrease with time as Frank found in his

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[1] Frank, op. cit., p. 62.

resistance measurements.[1] The error in parts per thousand, however, was found to remain fairly constant.

The 1-iodo-2,4-dinitrobenzene used in this study was prepared simply by refluxing a mixture of sodium iodide and 1-chloro-2,4-dinitrobenzene in N-N'-dimethylformamide for 15 minutes. The product was collected from an ice-water mixture and recrystallized from 95 per cent ethanol. The melting point range was 86-89° C. The reaction between 1-iodo-2,4-dinitrobenzene and piperidine in 95 per cent ethanol was carried out at three temperatures. Since 1-iodo-2,4-dinitrobenzene is not as soluble in 95 per cent ethanol as the chloro homolog, different concentrations were used than had been used in the above reaction with the chloro homolog. A Sargent Mecurial Thermoregulator was employed to keep the water bath at the desired temperature and proved to be very successful. A new procedure was followed for the reaction at 0.1° C. which permitted several runs to be made in a shorter period of time with a minimum of error.

An increase in the conductance ratio was found to be directly proportional to the time. The slope of the line obtained allowed the calculation of the reaction rates and half-lives of the reaction. The reaction rates at several temperatures was used to calculate the activation energy and change in entropy. The rate constants for the

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[1] Ibid., p. 66.

1-iodo-2,4-dinitrobenzene reaction with piperidine were found to be 0.0558, 0.3598, and 1.007 liters mole^{-1} minutes^{-1} for 0.1° C., 25.0° C., and 40.0° C., respectively. The energy of activation, as calculated from the integrated Arrhenius equation was 12.28 Kcal. The change in entropy was -19.25 calories degree^{-1} mole^{-1}.

The reaction between 1-bromo-2,4-dinitrobenzene and piperidine in 95 per cent ethanol was followed conductometrically at three temperatures. This reaction also yielded a linear relationship between the conductivity ratio and the time. From the slope if this line, the specific rate constants and half-lives were again determined. The rate constants were 0.2748, 1.588, and 4.216 liters mole^{-1} minute^{-1} for the temperatures 0.1° C., 25.0° C., and 40.0° C., respectively. From the specific rate constants at different temperatures, the energy of activation was calculated to be 11.59 Kcal. The change in entropy was found to be -18.74 calories degree^{-1} mole^{-1}.

The reactivity series for the 1-halo-2,4-dinitrobenzene with piperidine in 95 per cent ethanol was found to be Cl > Br >> I by a conductometric method. Only the 1-chloro-2, 4-dinitrobenzene with piperidine has been reacted and studied by a non-conductometric process in 95 per cent ethanol.

For other problems to be studied conductometrically, a list of reactions that have been studied by chemical analysis have been placed in Chapter III of this work. Also, solvent effects on the same series might be tried to see if they have an effect on the rate constants and order of reactivity among the halogens.

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